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An Investigation of Low Degree of Substitution Carboxymethylcelluloses

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AN INVESTIGATION OF LOW DEGREE OF SUBSTITUTION CARBOXYMETHYLCELLULOSES

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INTRODUCTION

The hydroxyl groups of cellulose play an important role in the pronounced affinity of cellulose for water and in the bonding of cellulose fibers in the formation of paper. Several investigators have studied cellulosic pulps in which varying amounts of these hydroxyl groups have been substituted with hydrophobic groups such as the methoxyl or acetyl group. They found that at low degrees of substitution (D.S.) the affinity for water of these substituted celluloses and the physical strength of handsheets formed from these substituted celluloses were increased, due perhaps to an opening up of the cellulose structure making more cellulosic hydroxyl groups available for bonding and the adsorption of water. As the D.S. was increased the affinity of the product for water and the physical strength of handsheets formed from the substituted pulps decreased rapidly due to the replacement of more and more of the hydroxyl groups with the hydrophobic acetyl or methoxyl groups.

If hydrophilic groups instead of hydrophobic groups are substituted for the cellulosic hydroxyls the resulting pulp should have properties that differ from the properties of both the original pulp and the pulps mentioned in the preceding paragraph. At low D.S.'s the increase in affinity for water of the substituted pulps should be greater and this increase should be retained at higher D.S.'s. The physical strength properties of handsheets formed from a pulp substituted with hydrophilic groups should also be increased.

For this study the carboxymethyl group was chosen for the substitution of cellulose pulps because of its hydrophilic nature and because some of the properties of carboxymethylcellulose and its preparation have been reported by other investigators. Most of their work, however, deals with soluble carboxymethylcelluloses (CMC) of high D.S.'s (D.S. greater than 0.3), while in this study it was necessary to retain the insoluble fibrous nature of the cellulose pulps.

In this thesis a method is developed for the preparation of low-D.S. CMC pulps, retaining the fibrous nature of the pulp, without excessive degradation. Some of the physical strength properties of handsheets formed from these carboxymethylated pulps are also determined.

LITERATURE REVIEW

The historical review for this study will be divided into two sections: (a) a review of some of the chemical treatments that have been used to change the physical properties of cellulosic pulps, and (b) a review of the literature on CMC.

CHEMICAL TREATMENT OF PULPS

In order to achieve a better understanding of the mechanism of beating and bonding or to improve the properties of pulps and papers various investigators have chemically treated and altered cellulose fibers.

Partial methylation of an unbleached sulfite pulp was carried out by Jayme and Froundjian (1). The methoxyl content of the pulp was increased from 1.59 to about 9%. When this methylated pulp was beaten, the handsheets formed were 50% stronger in bursting strength than the sheets from the unmethylated pulp. Various tests were carried out to measure the water-binding capacity or hydrophilic properties of the treated and untreated pulps. It was found that the partially methylated pulp bound about 0.5 mole more water per mole of cellulose (50% increase) than the nonmethylated pulp. It seems likely that these changes were due to an opening up of the cellulose structure upon methylation that left more cellulosic hydroxyls available for water-binding and bonding.

In order to study the role of cellulosic hydroxyl groups in papermaking, Bletzinger (2) prepared a series of cellulosic pulps with increasing amounts of the hydroxyl groups covered with hydrophobic acetyl groups. He prepared a series of pulps with acetyl contents from 4.25 to 26.46% by a method which

does not degrade the pulp or change its fibrous nature. When handsheets were made from these unbeaten pulps, the strength properties of the sheets decreased as the acetyl content increased. Even an acetyl content of 4 to 6% was enough to reduce the wettability of the fibers and the strength of the resulting sheets. When these pulps were beaten, however, it was found that fibers with acetyl contents below 8 to 9% formed sheets with strength properties greater than sheets prepared from untreated fiber with a maximum burst increase of about 10%, at an acetyl content of about 6%. Above an acetyl content of 8 to 9% the strength properties of the beaten pulp fell off rapidly until at higher acetyl contents water would no longer wet the fibers.

The following explanation was offered by Bletzinger (2) for the behavior of the acetylated fibers. For the unbeaten fiber the substitution of any external hydroxyl groups reduced the number available for bonding and consequently lowered the resulting sheet strengths. Acetylation does, however, alter or loosen the internal structure of the fiber due to the size of the acetyl group. On beating, this loosened fiber structure favors the development of external surface. Thus, after beating a pulp of low acetyl content there were more hydroxyl groups available for bonding than in the untreated pulp. As the acetyl content was increased (above 8 to 9%) and more hydroxyl groups were covered, the fibers became more hydrophobic in nature, and the strengths of the resulting handsheets decreased. When these pulps of higher acetyl contents were beaten in acetone and handsheets formed in acetone, the resulting handsheets had strength properties superior to the untreated pulp processed in water. It was assumed that the solvating action of the acetone on the acetyl groups was similar to the relationship between water and cellulosic hydroxyls in untreated cellulose.

Aiken (3) confirmed the results of Bletzinger using another rag stock and a bleached Mitscherlich pulp. Using a milder acetylation procedure to obtain the pulps of low acetyl contents, he found a maximum increase in strength properties for the acetylated rag stock at an acetyl content of about 3%. At this point, comparing pulps beaten for 45 minutes in the Lampén mill, he observed an 80% increase in burst and a 40% increase in tensile. Aiken also measured the hygroscopicity of dried acetylated pulps and found a maximum at an acetyl content of about 3%. The curves of bursting strength *versus* acetyl content and hygroscopicity *versus* acetyl content were found to be very similar. These results were interpreted in a manner similar to the interpretations by Bletzinger.

Aiken also added xylan and acetylated xylan to rag stocks. He found that while the addition of xylan resulted in an increase in the strength properties of the resulting sheets, the acetylated xylan caused a decrease in the strength properties. It is assumed that the increase in strength achieved by the addition of noncellulosic carbohydrates, such as xylan, is due to the mutual bonding of the hydroxyls of these carbohydrates and those of cellulose. When these hydroxyl groups are covered by acetylation, as was done by Aiken, their addition to a pulp slurry can no longer increase the degree of bonding.

Harrison (4) confirmed the results of Bletzinger and Aiken. He also prepared butyryl and stearoyl cellulose derivatives of varying substitution. With these acyl derivatives the hygroscopicity and physical strength properties of the substituted pulps were decreased even at very low D.S.'s.

These investigators (1-4) have shown that by partial methylation and partial acetylation of cellulose pulps it is possible to increase

appreciably both the strength properties of paper formed from the pulps and the hygroscopicity of the pulps. This change in properties is probably due to an opening up of the cellulose structure during partial methylation or acetylation, resulting in the availability of more cellulosic hydroxyls for bonding and the adsorption of water.

Clark (5, 6) has suggested that the strongest bonds between cellulose chains are due to linkages in which a primary hydroxyl group is involved. Further, he suggested that in many cases water alone cannot break these linkages, but that their conversion to ether and ester groups may disrupt the linkages. If most of the secondary hydroxyls are left intact the resulting substituted pulp would be more hydrophilic. Clark stated further that (5),..."if methylation or acetylation or the addition of other similar hydrophobic groups extends to the majority of the secondary hydroxyls, then the structure becomes hydrophobic." "The introduction of additional carboxylic or other hydrophilic groups (if this is possible), of course, would not affect the hydrophilic nature of the product." It is known, however, that high-D.S. CMC is water soluble and in this study low-D.S. CMC was found to have higher equilibrium moisture contents than unsubstituted cellulose.

The physical properties of pulps also depend on their chemical composition. It has been shown by several investigators that the hemicellulose contents of wood pulps play an important role in their beating and strength development. An excellent review of "The Influence of Hemicelluloses in Wood Pulp Fibers on Their Papermaking Properties" has been presented by Cottrall (7).

Several investigators, among them Jayme and Lochmüller-Keler (8), March (9), and Ratliff (10), have prepared pulps of varying hemicellulose contents and found that pulps with higher hemicellulose contents beat faster and form sheets of higher burst and tensile strengths than pulps of lower hemicellulose contents. Cottrall (7) in his review gave beating, strength, and opacity data for a strong bleached sulfite pulp before and after extraction with 7% caustic soda to remove most of the hemicelluloses. The unextracted pulp beat faster to a given freeness value and had higher burst and tear values at a given freeness or beating time. The opacity of the unextracted pulp was reduced much more rapidly with beating than was the opacity of the extracted pulp. Cottrall presented the theory that the major difference between these two pulps was in their plasticity. The unextracted pulp adsorbed more water and swelled more due to the hydrophilic nature of its high hemicellulose content. This increased swelling resulted in an increased plasticity of the fibers which favored fibrillation rather than cutting of the fibers upon beating.

Most of the explanations offered for the role of hemicellulose in beating are similar to that presented by Cottrall. The hemicelluloses, due to their hydrophilic nature, cause a pulp fiber to adsorb more water and swell to a greater extent. Also the hemicellulose, being a part of the fiber, introduces a point in the fiber where it is easier for fibrillation to take place. Further, the hydroxyl groups of the hemicelluloses are available for bonding in addition to the cellulosic hydroxyl groups.

Rag pulp, in spite of their lack of hemicellulose, form papers of considerable strength. Cottrall (7) attributed this strength to the

structure of rag fibers which permits the formation of a very large amount of fibrillation after extensive beating. Rag pulps require considerable treatment in both the breakers and the beaters before a pulp suited for papermaking is obtained. Cottrall (7) has noted that:

> Wood pulp is naturally plasticized by the hemicelluloses it contains and this facilitates fiber-to-fiber bonding which can then be augmented by the beating action. Rag pulp, on the other hand, relies solely on being plasticized mechanically by the beating action and consequently, requires the latter to be prolonged to a considerable extent before it achieves similar results to those achieved by wood pulp with relatively moderate treatment.

It is also of interest for this study to note a remark made elsewhere by Cottrall (11):

> If you could introduce hemicellulose in pulp and chain it up to the fiber, as it were, I think then you would get this increased strength. If you could get some sort of sticky colloid which was not soluble in water and was entrapped with the fiber, I think you would get increased strength of paper in that way.

Dixson (12) realizing the importance of the cellulose-water relationship in beating and bonding studied the effect of surface-active agents, which alters this relationship, on beating and sheet strength. He found that the adsorption of hydrophobic material by the fibers decreased the amount of fiber-to-fiber bonding, producing handsheets with greatly reduced physical strength properties. He also found that by treating a fiber slurry with locust bean gum, cellulose gel, or gelatin it was possible to increase the hydrophilic character of the pulp and the strength of the sheets made from the pulp.

The addition of nonfibrous materials to pulp in the beater in an attempt to improve strength properties has been known for some time. The most common beater additive is probably starch, although other naturally occurring polysaccharides, cellulose derivatives, and synthetic resins have been found useful in this field. A survey of the beater additive literature has been published by Jayme and co-workers (13).

The role of beater additives in achieving higher strength properties varies for the different materials used. Many beater additives are deflocculating agents and as such may cause more uniform beating and sheet formation. Of the more commonly used beater additives many are carbohydrate gums and may act as cementing material in the fibrous structure. The hydroxyl groups of these carbohydrate materials may aid in fiber-to-fiber bonding through bonding with the cellulosic hydroxyls.

Methycellulose and CMC are the two cellulose derivatives most widely used as beater additives. According to Leech (14) and Horsey (15) these materials aid in both the formation of the sheet, because of their deflocculating properties, and in fiber-to-fiber bonding because of their free hydroxyl groups.

Both Horsey (15) and Edge (16) have published articles on the effect of CMC as a beater additive on the physical properties of the resulting sheets. Horsey found that the addition of 5% of CMC to the beater brought about an increase in the general strength and sizing properties of sheets formed at high freeness. At lower freeness it was found that the opacity and porosity of the sheets were decreased by the addition of CMC. Thus, the amount of beating required to obtain a given strength, opacity, or porosity was decreased by the addition of CMC.

PROPERTIES OF CARBOXYMETHYLCELLULOSE

Carboxymethylcellulose (CMC) has become one of the better known cellulose derivatives. It has many and varied uses based on its properties as a protective colloid, a thickening agent, and a film-former (17). The largest use of CMC is as a builder in synthetic detergents (several million pounds annually). In this field, due to the protective colloid nature of CMC, it is utilized as a soil-suspending agent to prevent soil redeposition from wash waters (18). CMC is also used industrially in foods, paints, textiles, and drilling muds (18). As mentioned earlier, CMC is used in the paper industry as a beater additive and is also used as a sizing agent to increase the printability and gloss of some grades of paper and board.

Commercial CMC is used in various degrees of purity and in various D.S.'s from about 0.3 to 1.5. In this range it is water soluble and usually used in the sodium salt form (the free acid is insoluble in water). Commercially these CMC products are prepared continuously or in batch operations by successively soaking a high alpha-cellulose wood pulp or a cotton linters pulp in aqueous solutions of strong caustic soda and sodium monochloracetate. The CMC is then precipitated and sold or may be purified to remove the sodium glycolate and sodium chloride that are by-products of the preparation.

Although several patents have been issued for the commercial preparation of CMC (19-24) they differ chiefly in reaction conditions, apparatus used, and methods of precipitation and purification. Some of the variables in the preparation of CMC have been investigated by McLaughlin and Herbst

(25) and Daul and Reinhart (26). Klug and Tinsley (27) obtained a patent on the preparation of CMC in an alcoholic reaction medium of at least 1.5 parts of alcohol for each part of water. The alcoholic reaction medium maintained the CMC formed in an insoluble form and permitted more complete reaction and easier washing of the final product.

Several studies of the position and uniformity of substitution in CMC have been published recently (28-35). The most complete investigation has been made by Timell (28-32), and an excellent survey of both his work and the work of others in the field is to be found in his latest article on the subject (32). A brief summary of the results of this work follows.

It was shown that substitution of one of the secondary hydroxyls on a cellulosic glucose residue inhibited the substitution of the other secondary hydroxyl. Thus, 2, 3, or 2, 3, 6 substituted glucose residues did not exist in CMC unless products of very high D.S.'s were prepared.

Although there was some difference of opinion (32, 33), it appeared that the primary hydroxyl group was about twice as reactive as the average of the two secondary hydroxyls. The 2-hydroxyl group seemed to be more reactive than the 3-hydroxyl group. Experiments by Timell (32) showed that the ratio of the number of substituted primary hydroxyls to substituted secondary hydroxyls was fairly constant at unity for CMC of D.S.'s from 0.075 to 0.36. Further, there was no trend in this ratio with D.S. to indicate any different relationship at lower D.S.'s.

Timell (32) has extracted with water a series of CMC samples of D.S.'s from 0.075 to 0.36. He found that for each sample the soluble portion had an appreciably higher D.S. and lower intrinsic viscosity than the original

sample or the insoluble portion. He also found that the water-soluble, higher D.S. fraction had the same ratio (unity) of substituted primary hydroxyls to substituted secondary hydroxyls as did the original sample. Thus, although portions of the cellulose were more highly substituted than other portions, the relative reactivity of the primary and secondary hydroxyl groups in these regions remained the same.

Daul, Reinhart, and Reid (26, 36-38) have studied CMC products from a D.S. of 1.8 down to a D.S. of 0.015. These workers have prepared CMC filaments, yarns, and cloths and have studied some of their physical properties of interest to the textile industry. Their method of preparation was successively soaking the cellulose sample in aqueous chloroacetic acid solutions and concentrated (30 to 50%) aqueous sodium hydroxide solutions. If the fibrous nature of a sample of high D.S. was to be maintained, methyl or ethyl alcohol was used to wash the product.

In one study (26) a series of CMC threads were prepared in the D.S. range from 0.015 to 0.100. The tensile strength of these threads increased as the D.S. was increased until a maximum increase of about 25% was obtained. At higher D.S.'s (above 0.150) the tensile strength of the threads began to decrease, possibly due to the removal of some slightly soluble material. In an earlier publication Reid and Daul (36) had noted that even at very low D.S.'s (D.S. = 0.025) the degree of swelling in water was increased for CMC yarns. They also noted that at a D.S. of about 0.07 the CMC yarns became slightly gelatinous when water-wet with a corresponding decrease in the wet-tensile strength of the yarns.

Daul, Reinhart, and Reid (26, 36-38) have observed increased tensile strength, swelling, and water adsorption in cotton threads and yarns that had been partially carboxymethylated. The uses suggested for these materials were in permanently sized fabrics for shirts, blouses, and clothing where the crisp hand and slightly starched feel of cloth produced from CMC thread would be desirable. Also, a resin treatment to produce crease-resistant cloth was facilitated when partly carboxymethylated cotton cloth was used. It was also noted that the carboxymethyl groups increased the soiling resistance of the cloth and changed its dyeing characteristics so that novel dyeing effects were possible. Some of the metal salts of low-D.S. CMC cloths were found to have considerable resistance to microbiological attack.

STATEMENT OF THE PROBLEM

The work reported in this thesis has as its goal the study and development of a reproducible method of preparing low-D.S. CMC pulps retaining the fibrous nature of the original cellulose pulp and the determination of some of the papermaking properties of the CMC pulps so prepared. Since the papermaking properties of the resulting pulps are of interest in this thesis it was necessary to avoid mercerization of the pulps and to keep degradation to a minimum in their preparation. In order to retain the insoluble fibrous nature of the original pulp, the D.S. range of interest in this study is from 0 to 0.1, a range of substitution up to one carboxymethyl group for every ten glucose residues in the pulp.

EXPERIMENTAL PROCEDURES

RAW MATERIALS

Early experiments for this thesis were carried out using alkali-washed and bleached cotton linters obtained from the Hercules Powder Company. These first experiments included: (a) preparation of samples for the development of an accurate method for the measurement of D.S., (b) initial attempts to develop a suitable method of CMC preparation, and (c) further study of this method of CMC preparation.

Since the papermaking properties of CMC pulps were of interest in this thesis a paper-grade rag pulp was used for the remainder of the work. Bletzinger (2) and Aiken (3) in their acetylation studies used a rag stock supplied by a local rag paper mill. This pulp was chosen because of its high degree of polymerization and its low content of noncellulosic material. A similar type of material was used in this investigation. A local rag paper mill supplied 50 pounds of their No. 1 hard rag stock prepared from unbleached, muslin-grade rags. This pulp had been prepared in a special laboratory scale run but the lime cook and hypochlorite bleach which the pulp received were equivalent to a mill scale run. This pulp was received in the wet condition, containing about 75 to 80% water, and was stored in Pliofilm bags for a maximum of one week before being treated as described in the following paragraphs.

Bletzinger (2) and Aiken (3) found that the fibers of the original rag stock were too long to be handled satisfactorily in laboratory beating and sheetmaking equipment. They found that this difficulty could be overcome by cutting the rag stock in a laboratory beater for a short time at a

very low consistency. Bletzinger treated his pulp for five minutes at a consistency of 0.3% in the 5-pound capacity Valley beater with 25 pounds on the bedplate. The Schopper-Riegler freeness dropped to between 710 and 725 cc. Aiken used the same conditions and beater for seven to eight minutes and obtained freeness in the same range. In both cases the cut rag stock was entirely satisfactory in sheetmaking and strength characteristics as well as chemical activity.

A preparation of the original rag stock similar to that used by Bletzinger and Aiken was used in this investigation. The 5-pound capacity Valley beater was not available for this treatment, so the 5-pound capacity Noble and Wood beater was used. Two preliminary runs were made at 0.3% consistency and with a bedplate loading of 200 pounds. The results are given in the following table:

TABLE I

PRELIMINARY BEATER RUNS

Run 1

Beating Time, min.	0	1	2	3	4	5	6	7
S.-R. Freeness, cc.	850	830	760	670	550	450	350	300

Run 2

Beating Time, min.	1/4	1	1-1/2	2	2-1/2
S.-R. Freeness, cc.	850	830	790	770	720

To provide a supply of raw material for further investigation, 28 pounds of the rag stock were cut at 0.3% consistency for 2-1/4 minutes in the 5-pound capacity Noble and Wood beater with 200 pounds on the bedplate (64 runs of 0.435 pounds of pulp each). Periodic tests showed that the Schopper-Riegler freeness of the pulp varied from 720 to 740 cc. The cut pulp was partly dewatered by draining on a cloth-covered wash box and was

then transferred to an experimental blow tank where it was mixed for three hours with a 1 H.P. Unipower agitator and for an additional three hours with both the Unipower agitator and a 1/4 H.P. Lightnin' mixer. The pulp was allowed to drain overnight, dewatered on a desk-top Buchner, shredded, and spread to air dry. When the pulp was dry it was placed in Pliofilm bags for storage. This pulp will be referred to in this thesis as standard rag pulp.

Twenty-five additional runs, identical to those mentioned above, were made in the Noble and Wood beater. Due to the size of the blow tank, this pulp could not be randomized with the pulp mentioned above. This pulp was used for preliminary experiments and will be referred to in this thesis as nonrandomized rag pulp.

The remaining untreated pulp was broken by hand into small pieces and spread to air dry. This pulp was placed in Pliofilm bags and stored for emergency use.

DETERMINATION OF DEGREE OF SUBSTITUTION

Two methods of determining the D.S. of CMC samples were investigated for this thesis. The first method studied was the copper-salt method outlined by Reid and Daul (36), Conner and Eyler (39), and Hoffpauir and O'Conner (40). In this method a sample of the free acid of CMC was soaked overnight in an excess of 2% aqueous cupric sulfate in order to form the cupric salt of the CMC. The following morning the excess cupric sulfate was washed from the pulp by several washes with 50% methyl alcohol followed by two washes with absolute methyl alcohol. The pulp sample was then oven dried at 50°C. and weighed. The copper content of the weighed sample was determined iodimetrically after the pulp had been digested with strong acid.

This method of analysis was sufficiently accurate for the low-D.S. CMC samples of interest in this thesis, but the time and care required did not make it suitable as a routine method.

The copper salt of CMC has the blue color of the copper ion and this color persists after several washes with water or 50% methanol. To determine if a sample had been carboxymethylated, it was soaked 10 to 15 minutes in 2% cupric sulfate and water-washed. The presence of a blue color indicated that the sample had been substituted, and the intensity of the color was an approximate indication of the D.S.

A second method of determining the D.S. of CMC samples was studied. The silver salt of CMC was formed by treating the sample with a silver-o-nitrophenolate solution. The amount of silver combined was determined by titrating aliquots of the silver-o-nitrophenolate solution by the Volhard method before and after contact with the sample. This method has been used by Sookne and Harris (41) to determine the base-combining capacity of cotton, and by Elizer (42) to estimate the carboxyl content of oxidized starches. It was adopted as the standard method for this investigation.

To prepare the silver-o-nitrophenolate solution used in this method, one liter of distilled water was heated to about 60°C.; 15 grams of o-nitrophenol and 15 grams of silver oxide were added, and the mixture was stirred for about 30 minutes. This mixture, when allowed to cool, formed a saturated silver-o-nitrophenolate solution (about 0.01 molar) with a hard cake of excess silver-o-nitrophenolate at the bottom of the reagent flask. This cake was used to form fresh solutions simply by the addition of water and heating to 60°C. A standardized potassium or ammonium

thiocyanate solution (about 0.01 molar), a saturated indicator solution of ferric ammonium sulfate, and boiled dilute nitric acid were also required.

In this method it was necessary that the CMC be in the free acid form. In most of the preparations, acidification of the CMC with dilute hydrochloric or acetic acid was included as a step in the preparation, but for CMC samples obtained in the salt form an initial soak in dilute acid was required before the determination. In either case, the sample was washed extensively with distilled water in order to remove any impurities or excess acid. The sample was then washed twice with absolute methyl alcohol and oven dried overnight at 50°C. Moisture determinations on the dried samples were made only for CMC preparations 36 to 43, and for these samples the moisture content varied from 1.7 to 2.3%. Since these values are very low, the error incurred by not determining the moisture content of every sample was small.

Duplicate or triplicate samples of the ovendry pulp weighing approximately 0.5 grams were accurately weighed out and transferred to 125-cc. stoppered flasks. Into each flask 50 cc. of the silver-o-nitrophenolate solution were pipetted; the flask was stoppered securely, swirled, and set aside overnight. Blank determinations were run in triplicate.

The next morning 25 cc. of the clear supernatent liquid from each of the flasks were pipetted into clean 125-cc. flasks, and 5 cc. of dilute nitric acid, 2 to 3 cc. of ferric-alum indicator, and 2 to 3 cc. of nitrobenzene were added. The solution was then titrated to a reddish tinge with the standardized thiocyanate solution mentioned earlier. The blank solutions were handled in an exactly similar manner. The results were reported as D.S. calculated as shown in Appendix I.

This method has been entirely satisfactory for this thesis. The values obtained for D.S.'s agreed well with those obtained by the copper-salt method and the reproducibility for any given sample was excellent. The maximum variance in D.S. value for duplicate samples run on the same day or on different days was about 5%. An analysis of the uncarboxymethylated standard rag pulp by this method gave an apparent D.S. value of 0.002.

DETERMINATION OF VISCOSITY

Initial attempts to determine the viscosity of pulps in this thesis were unsuccessful due to difficulty in obtaining a solution of the rag pulp in cupriethylenediamine solution. After some experimentation, the following methods of sample preparation and solution in cupriethylenediamine were found to give satisfactory results: The pulp sample was thoroughly washed with distilled water and then defibrated for one minute in a water suspension in an Oster fountain mixer. The sample was then filtered, suspended in absolute methyl alcohol for 15 minutes, and returned to the mixer for 15 seconds. The methyl alcohol was replaced with fresh absolute methyl alcohol in which the pulp was soaked for 15 minutes. The alcohol was removed from the pulp by filtration. The pulp was suspended in benzene, allowed to soak for one hour, and returned to the mixer for 30 seconds. The benzene was replaced with fresh benzene in which the pulp was soaked for one hour before the benzene was removed by filtration. The pulp was spread to air dry overnight and then stored in closed weighing bottles over calcium chloride in a desiccator.

Samples of the prepared pulp were accurately weighed out and placed in

60-ml. serum bottles fitted with "pullover" type rubber stoppers. Three glass beads were added to each bottle and enough 0.04% Nacconol NR solution (wetting agent) was pipetted into each bottle to make a suspension of exactly twice the concentration desired in the final solution. The bottles were stoppered and placed in a horizontal reciprocating shaker for one hour. At the end of this period an amount of stock cupriethylenediamine (1.0 molar) equal to the amount of Nacconol solution already present was added to the serum bottles by the method of Browning et al. (43). This method entailed the alternate evacuation of the serum bottle by means of a water aspirator and filling with purified nitrogen (at least three times). After the final evacuation, the measured amount of cupriethylenediamine was introduced into the bottle and the bottle filled with purified nitrogen. The bottles were returned to the shaker for one hour after which they were transferred to a 25°C. water bath to await viscosity measurement. Viscosities were determined in calibrated Ostwald-Fenske viscosity pipets to which the solutions were transferred by means of a hypodermic syringe. The viscosity of the 0.5 molar cupriethylenediamine used as a solvent was also determined each day.

Two methods of interpreting viscosity data were used in this thesis. For most of this study the solution viscosity of a pulp was determined at only one concentration. A sample of approximately 0.125 grams was accurately weighed out and equal amounts of Nacconol solution and cupriethylenediamine were added to bring the final cellulose concentration to 0.25 grams per 100 cc. Moisture determinations were made on some of the early samples and the values were between 2.5 and 5.5%. For the remainder of the study a moisture content of 4% was assumed as the observed variation

in moisture content did not significantly affect the D.P.'s calculated as in Table II. Thus, the concentration of the solution adjusted for the moisture content of the pulp was 0.24 grams per 100 cc.

In order to interpret viscosity differences in terms of degree of polymerization the following table was prepared giving approximate relationships between observed viscosities, relative viscosities, intrinsic viscosities, and degrees of polymerization.

TABLE II

APPROXIMATE RELATIONSHIP BETWEEN MEASURED VISCOSITY AND D.P.

Efflux Time, sec. A	Relative Viscosity B	Intrinsic Viscosity C	Approximate D.P. D
650	9.14	12.7	2160
600	8.43	12.0	2040
550	7.74	11.2	1900
500	7.03	11.0	1870
450	6.33	10.5	1780
400	5.62	9.6	1630
350	4.92	8.8	1500
300	4.22	7.8	1320

A) As measured at 0.24g./100 cc. concentration.

B) Calculated from column A using a solvent efflux time of 71.1 sec.

$$\eta_{rel.} = \frac{\text{solution efflux time}}{71.1}$$

C) Determined from column B using a nomograph of Martin's Equation.

$$\eta_{rel.} = 1 + [\eta]\, Ce^{0.30C[\eta]}$$

D) Calculated from column C using equation:

$$D.P. = K[\eta] \text{ with } K = 170$$

For the final CMC samples (CMC preparations 36 to 43) the moisture content of each sample was determined and the viscosity of each sample was determined at four different concentrations between 0.05 and 0.25 grams per 100 cc. The specific viscosity and the reduced viscosity were calculated at each concentration.

η_{sp} = specific viscosity,

$$= \frac{\text{viscosity of solution - viscosity of solvent}}{\text{viscosity of solvent}}$$

$\eta_{sp/C}$ = reduced viscosity

where C = pulp concentration in grams per 100 cc.

In order to obtain the intrinsic viscosity and consequently the D.P. of each sample the logarithm of the reduced viscosity was plotted versus the concentration (see Figure 5, page 53). The intrinsic viscosity (intercept with the viscosity axis) was converted to D.P. by multiplying by 170 (see Table XI, page 49).

These two methods of evaluating viscosity data were used for samples of CMC although the equations and relationships involved have been derived only for pure cellulose. It was felt that the electrolytic nature of the carboxymethyl groups would not appreciably affect the measured viscosity due to the very low D.S.'s of the pulps in this study. Further, Trap and Hermans (44) have shown that even for CMC of higher D.S.'s dissolved in aqueous solutions of high electrolyte contents, the viscosity is the same as for an unchanged polymer due to the low charge density of the CMC.

DETERMINATION OF MERCERIZATION

The iodine adsorption method used in this thesis to determine if a pulp sample had been mercerized is similar to a method described by Marsh (45). This analysis is based on the increase in iodine adsorption of a cellulose sample brought about by mercerization.

The determination was carried out as follows: The sample to be analyzed was ground to pass a 20-mesh screen in the micro-Wiley mill and then oven dried at 50°C. A 0.3000-gram sample of the dried pulp was accurately weighed into a 15 by 50 mm.-weighing bottle. A solution consisting of 40 grams of potassium iodide and 5 grams of iodine dissolved in 50 cc. of water was prepared and 1.2 cc. were pipetted into the weighing bottle containing the sample. The iodine-pulp mixture was kneaded using a glass stirring rod and was then transferred quantitatively to a 100-cc. volumetric flask. A saturated solution of sodium sulfate was used to transfer the pulp and to dilute the contents of the flask to exactly 100 cc. The flask was allowed to stand for one hour with frequent agitation. At the end of this period the contents of the flask were transferred to a centrifuge jar and centrifuged for 10 minutes at 2000 revolutions per minute. A 75-cc. portion of the clear supernatent liquid was pipetted into an Erlenmeyer flask and titrated to a starch end point with standardized N/50 potassium thiosulfate solution. A sample of the original iodine solution was also titrated with thiosulfate. The results of this analysis were recorded as the difference between these two titrations or the amount of iodine adsorbed by the pulp.

In order to calibrate this method, a series of pulp samples were treated at room temperature with aqueous sodium hydroxide solutions varying in concentration from 0 to 20%. The iodine adsorption of each sample was determined by the method outlined above. The samples that had been treated with sodium hydroxide solutions of a concentration greater than 13% (mercerized samples) each adsorbed more iodine than the samples that had been treated with sodium hydroxide solutions of concentrations less than 11% (unmercerized samples). The sample treated with 12% sodium hydroxide had an intermediate value. This difference in the amount of iodine adsorbed by the mercerized and unmercerized samples was reproducible (0.30-0.37 equivalents/gram). The amount of iodine adsorbed by a given sample, however, varied from day to day. Efforts to determine the cause of this day to day variation were unsuccessful. When an unknown sample was to be analyzed, an unmercerized sample (treated with 4% sodium hydroxide) and a mercerized sample (treated with 16% sodium hydroxide) were run simultaneously as control samples. This method proved suitable for this thesis.

Later work by Lakstigala (46) has shown that some of this day to day variation in iodine adsorption was due to changes in the concentration of the saturated sodium sulfate solution used in the analysis. These changes were caused by variation in the temperature of the room in which the reagent was stored.

PREPARATION OF CARBOXYMETHYLCELLULOSE

A series of 43 CMC preparations were carried out. Often several samples were included in a given preparation. Several other experiments to determine the effect of certain variables on pulp viscosity and mercerization were also carried out. These experiments and preparations are discussed in the following pages.

INITIAL STUDIES

The first three CMC pulps in this study were prepared by soaking 100 grams of air-dried cotton linters in 300 cc. of an aqueous chloroacetic acid solution for five minutes, filtering off the excess acid solution, and soaking the pulp at room temperature in 800 cc. of approximately 35% aqueous sodium hydroxide. The CMC pulps were then acidified with dilute hydrochloric acid and washed thoroughly with distilled water. These three samples were used in the development of the methods for measuring D.S. The variables in these preparations and the D.S.'s obtained are given in the following table:

TABLE III

CMC PREPARATIONS FOR D.S. METHOD

CMC Preparation	$CH_2ClCOOH$ Conc., %	Reaction Time in NaOH, min.	D.S.
1	16.7	25	0.034
2	50.0	75	0.075
3	16.7	30	0.032

Although this method of preparation was used for the initial samples, it was unsuitable for the remainder of this study because of the use of mercerization-strength caustic. For this study CMC samples that have not been mercerized were desired because Probst (47) has shown that mercerization adversely effects the papermaking properties of pulps.

Carboxymethylation in a pyridine reaction medium was attempted (CMC preparations 4 to 8). It was hoped that the alkaline nature of the pyridine would eliminate the need for the use of caustic in the preparation. Cotton linters were suspended in pyridine solutions of chloroacetic acid and were allowed to stand at room temperature overnight or maintained at reflux temperatures for several hours. Similar experiments were also carried out replacing the chloroacetic acid with sodium chloroacetate. No substitution occurred in any of these experiments.

An attempt (CMC preparation 9) to obtain CMC by soaking cotton linters overnight in an aqueous solution of sodium chloroacetate at a pH of 10.5 was unsuccessful.

In CMC preparation 10, 20 grams of cotton linters were soaked for five minutes in 200 cc. of an isopropyl alcohol solution containing 30 grams of chloroacetic acid. At the end of this soak, 1 liter of an alcoholic sodium hydroxide solution (16.7% methyl alcohol, 83.3% isopropyl alcohol; 52 g./l. sodium hydroxide) was added to the mixture. This mixture was heated to boiling and maintained at reflux temperatures for five hours. The alcoholic solution was then removed by filtration; the pulp was acidified with dilute acetic acid, and was thoroughly washed with distilled water. The D.S. of the product was 0.009 (D.S. of untreated pulp is 0.002).

Although the method used in CMC preparation 10 was found to be suitable for this study, a different method was tried in CMC preparation 11. Fifty grams of cotton linters were suspended in 1700 cc. of solution consisting of 35 cc. of methyl alcohol, 1665 cc. of isopropyl alcohol, and 10 grams of sodium hydroxide. The mixture was heated to boiling and after refluxing for two hours, 15 grams of chloroacetic acid dissolved in 100 cc. of isopropyl alcohol were added. Reflux was continued for an additional six hours. The resulting pulp was soaked in dilute acetic acid and then thoroughly washed with distilled water. No substitution was obtained by this method.

In these initial preparation studies, substitution without the use of strong aqueous caustic was obtained only in CMC preparation 10. The method of preparation devised in this experiment and the CMC pulps prepared by this method are studied throughout the remainder of this thesis.

PREPARATION PROCEDURES

A uniform method of CMC preparation was used throughout this study. Although the conditions were changed as a better understanding of the method was obtained the basic procedure remained the same. In this way the results of different CMC preparations could often be compared and the laboratory handling of the samples was facilitated.

The preparation of CMC has been divided into four separate operations: (a) pretreatment, (b) acid treatment, (c) substitution, and (d) wash. In the following pages all of the studies of each operation are discussed together although they may have been carried out at widely separated times in the over-all investigation. It was felt that by presenting the results

in this manner a better understanding of the effects of each variable may be obtained.

The procedures for each one of these four operations are given in the following paragraphs. These procedures are presented for the amounts of pulp used most frequently in this study. The amount of pulp used as a starting material in a given preparation, however, was sometimes varied. In instances where the amount of material used was different from that given in the following procedures the ratios of chemical to pulp were the same.

PRETREATMENT PROCEDURE

For this thesis two different raw materials and three different methods of pretreatment were used. For the initial experiments (through CMC preparation 18) air-dried cotton linters were used as a starting material. Although these cotton linters proved to be only slightly reactive, it was felt that the trends observed in their treatment would also exist when rag pulp was used. The cotton linters were used in the airdry form in all preparations except CMC preparation 17 in which one sample was washed with isopropyl alcohol and oven dried before treatment.

When the rag pulp was obtained and prepared as outlined in an earlier section, it was used for all of the remaining experiments. The nonrandomized rag pulp was used for CMC preparations 19 to 35 and the randomized, standard rag pulp was used for CMC preparations 36 to 43. There is no reason to suspect any difference in the chemical activity of the randomized and the nonrandomized rag pulps.

The rag pulp was not used in the original airdry form but was used after it had received one of two pretreatments.

Alcohol Pretreatment

A 250-gram sample of nonrandomized rag pulp was suspended in 2500 cc. of distilled water and placed in the cold room (40°F.) in a covered beaker for at least 18 hours. The sample was then diluted to 5 liters with distilled water and divided into two equal portions. Each portion was placed in the British disintegrator for 2500 revolutions. The pulp was then dewatered on a Buchner funnel and suspended in 3 liters of absolute methyl alcohol. After a 20-minute soak, the methyl alcohol was replaced with fresh absolute methyl alcohol and the pulp was allowed to soak for an additional 20 minutes. After one further exchange of alcohol and another 20-minute soak, the pulp was filtered and spread to air dry.

Alcohol-Benzene Pretreatment

The procedure for this pretreatment was identical with the alcohol pretreatment through the final filtration. Before drying, the pulp was suspended in 3 liters of pure benzene and allowed to soak for one hour. The benzene was then replaced with fresh benzene in which the pulp was soaked for another hour. The benzene was then removed by filtration and the pulp spread to air dry.

In the pretreatments for CMC preparations 34 to 43, 700 grams of pulp were used. In these pretreatments the pulp was defibrated in a Williams defibrator for one minute instead of in the British disintegrator. Except for this change these pretreatments were similar in every respect to the one outlined above.

ACID TREATMENT PROCEDURE

The acid treatment of a 5-gram pulp sample required soaking the sample 5 to 60 minutes in 40 cc. of an isopropyl alcohol solution containing 0 to 30% (grams per 100 cc. of final solution) chloroacetic acid. At the end of the soak period the excess chloroacetic acid solution was removed from the pulp by filtration on a Buchner funnel. The chief variables in this operation were the concentration of the chloroacetic acid solution and the length of the soaking period.

In CMC preparations 34 and 36 to 43, 700 grams of pulp were soaked for 30 minutes in 6 liters of an isopropyl alcohol solution containing 0 to 2% chloroacetic acid.

SUBSTITUTION PROCEDURE

The night before a CMC preparation, an excess of sodium hydroxide (80 grams per liter) was placed in a solution containing 12.5% methyl alcohol and 87.5% isopropyl alcohol (by volume). This mixture was placed on a rotator overnight. The excess undissolved sodium hydroxide was filtered off the next morning using Celite filter-aid. The alkali content of the clear alcoholic-caustic solution (about 60 grams of sodium hydroxide per liter) was determined by titration with standard acid.

Using this solution, 150 cc. of a 12.5% methyl- 87.5% isopropyl alcohol solution was prepared containing sufficient alkali to neutralize the chloroacetic acid retained by the pulp and yield an excess sodium hydroxide concentration of 0.1 to 3.0%. The acid-treated pulp was then added to this solution and the mixture was heated to boiling. The reaction mixture was boiled (78-82°C.) for one to four hours. The volume of the reaction

mixture was maintained constant by the addition of 12.5% methyl- 87.5% isopropyl alcohol to replace the amount lost by vaporization.

The chief variables in the substitution procedure were the concentration of the excess sodium hydroxide in the reaction mixture and the length of time the reaction mixture was maintained at the boiling point.

WASH PROCEDURE

At the end of the substitution reaction, the excess alcoholic sodium hydroxide was decanted from the slurry and the alcohol-wet, CMC pulp was neutralized with a dilute aqueous acetic acid solution. After about five minutes, the pulp was filtered on a Buchner funnel and suspended in distilled water. The sample was allowed to soak for about 30 minutes, was filtered on a Buchner funnel, and then resuspended in fresh water for another soaking period. This procedure was repeated several times for each CMC pulp. For CMC preparations 12 to 33, distilled water was used for all washes of the pulp, and after a sample had been thoroughly water washed it was prepared for D.S. or viscosity measurements by the procedures given in an earlier section. In CMC preparations 34 to 43, the neutralized pulp was washed with deionized water. Samples that were taken for D.S. and viscosity measurement, however, were given thorough washes with distilled water before being treated by the procedures mentioned earlier for these determinations.

In these final CMC preparations (34 to 43), the bulk of the pulp, after having been washed several times with deionized water, was placed overnight in 20 liters of a solution containing excess sodium bicarbonate

(about 60 grams per liter) in order to form the sodium salt of the carboxymethyl group. The following day the pulp was washed eight to ten times by soaking in deionized water for about 30 minutes, filtering, and resuspending the pulp in fresh deionized water. The deionized water was sufficiently alkaline so that there was little danger of again obtaining the acid form of the CMC. In these CMC preparations (34 to 43) the washed pulps were stored in Pliofilm bags in the cold room (40°F.) until used.

STUDY OF PRETREATMENT VARIABLES

The first study of the effect of pretreatment was in CMC preparation 17. In this preparation a sample of cotton linters that had been soaked in isopropyl alcohol and then oven dried at 50°C. (sample 17 B) and air-dried cotton linters (sample 17 A) were both used as starting materials. As is shown in Table IV, CMC was prepared from both of these samples in an identical manner. A higher D.S. CMC pulp was obtained from the sample that had been alcohol washed.

The rag pulp was received soon after these results were obtained and no further study of this effect upon cotton linters was made. In the first CMC preparation using rag pulp (CMC preparation 19), however, one sample was treated according to the alcohol pretreatment described earlier (page 30) while the remainder of the samples received no pretreatment. After the preparation had been completed and the samples were washed, the sample which had received the alcohol pretreatment, appeared to have a much higher D.S. than any of the other samples. This conclusion was based on the slimy feel of the pulp, the difficulty in filtering the pulp, and the intensity of the blue color of a portion of the pulp which had been soaked in 2%

cupric sulfate. The D.S. of this sample and the conditions of its preparation are given in Table IV (CMC preparation 19).

TABLE IV

EFFECT OF PRETREATMENT ON D.S.[1]

CMC Preparation	Pretreatment[2]	$CH_2ClCOOH$ Conc., %	Length of Acid Soak, min.	D.S.
17A	Water	37.5	10	0.016
17B	Alcohol	37.5	10	0.034
19	Alcohol	30.0	30	0.090
26A	Alcohol	5.0	30	0.025
	Alcohol	10.0	30	0.032
26B	Benzene	5.0	30	0.065
	Benzene	10.0	30	0.068

[1]Substitution reaction carried out by procedure given on pages 31 and 32 with a sodium hydroxide concentration of about 3.0% and a reaction time of four hours.

[2]See pages 29 to 31. All samples were water soaked. The pulp was then dried or solvent exchanged and dried from methyl alcohol or benzene as listed in the table.

This increase in the reactivity of a pulp after a water soak and re-drying from methyl alcohol is probably due to the less polar nature of the methyl alcohol. When a cellulose fiber is suspended in water there is a mutual attraction between the cellulosic hydroxyl groups and the water molecules. This attractive force together with the surface tension forces of the water cause the partial collapse of the fiber structure upon drying. A portion of this collapse is permanent but when the fiber is resuspended in water the cellulose structure swells with the recovery of some of its earlier porosity and reactivity. When the fiber is now dried from a less polar solvent such as methyl alcohol, the attractive forces between the cellulose and the solvent molecules and the surface tension forces of the

solvent are much smaller. Thus, when a cellulose fiber is dried from methyl alcohol the resulting fiber structure is more porous and more open to the penetration of solvents. The methanol-dried fibers are, therefore, more reactive and higher-D.S. CMC pulps are obtained.

The amount of structural collapse may be reduced still further in one of two ways. First, if the pulp had never been dried from water the irreversible collapse or hornification associated with this process would be avoided. Since all of the rag pulp had already been air dried from water this approach was not used in this thesis. The second method is to dry rewetted pulp from a nonpolar solvent such as benzene rather than from methyl alcohol.

Pulps dried from benzene were prepared according to the procedure outlined on page 30. CMC pulps of higher D.S.'s were obtained using samples of benzene-pretreated pulps than were obtained with alcohol-pretreated pulps. This is illustrated in CMC preparation 26 (Table IV) and by the difference between the D.S.'s obtained in CMC preparation 30 (alcohol pretreatment) and CMC preparation 31 (benzene pretreatment) as shown in Figure 1. These are merely two examples of this difference which was observed throughout this study.

The viscosities of pulps prepared from benzene-pretreated and alcohol-pretreated pulps were measured in later experiments (CMC preparations 30 and 31). CMC pulps of approximately the same viscosity were obtained using either alcohol or benzene-pretreated pulps.

Studies of the other preparation variables were made on both benzene and alcohol-pretreated pulps. For the final series of CMC preparations (CMC preparations 36 to 43), however, benzene-pretreated pulps were used since it was desired to obtain D.S.'s greater than were obtainable using alcohol-pretreated pulps.

STUDY OF ACID TREATMENT VARIABLES

The two main variables in the acid-treatment operation are the concentration of the chloroacetic acid solution and the length of the treatment period. Studies of the effect of the acid concentration on the D.S. of the resulting CMC pulps are outlined in Table V. The D.S.'s of the CMC products obtained in these preparations are given in Figure 1. The dependence of the D.S. obtained on the concentration of chloroacetic acid used may be seen in this figure. At low concentrations this relationship is almost linear, but as the acid concentration is increased the curves tend to level off so that a further increase in acid concentration no longer produces a corresponding increase in the D.S. The curves in this figure and in other figures in this report do not go through the point of zero D.S. The reason for this is that by the method of analysis used in this thesis the untreated rag pulp had a carboxyl content equivalent to a D.S. of about 0.002. The origin of these curves is therefore at this point. In Figure 1 it is seen that the initial slopes of the curves and the D.S. at which the curves level off vary for the different CMC preparations. Most of this variation is due to the use of different starting materials or different conditions as outlined in Table V. CMC preparation 20, however, deserves mention due to its lack of agreement with the remaining CMC preparations. The D.S.'s obtained in this preparation using alcohol-pretreated pulp were as high as

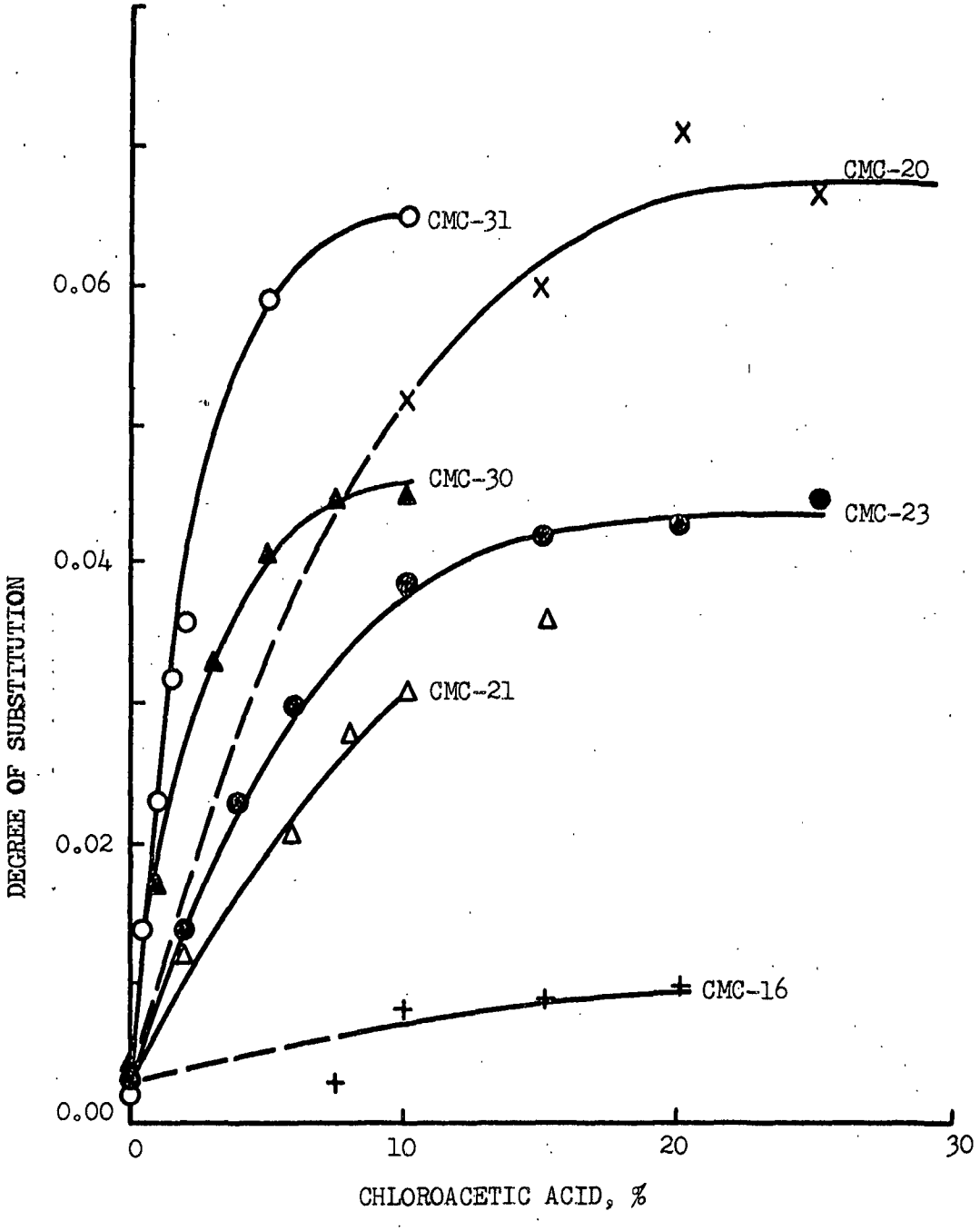

Fig. 1 Effect of Acid Concentration on Degree of Substitution

in other preparations using benzene-pretreated pulp. Isopropyl alcohol obtained from the Matheson Chemical Company was used in all of these preparations except CMC preparation 20. In preparation 20, due to a shortage in supply, isopropyl alcohol bottled and analyzed by the J. T. Baker Chemical Company was used. Although this change did not seem to be significant at the time, a later experiment (CMC preparation 32) was carried out using each of these brands of alcohol on separate samples under identical conditions. Significantly higher D.S.'s were obtained with samples in which Baker isopropyl alcohol was used as a reaction medium. The reason for this difference is not known, and since a large quantity of Matheson isopropyl alcohol had already been obtained it was used in all of the preparations except the two mentioned above (20 and 32).

TABLE V

STUDIES OF THE EFFECT OF ACID CONCENTRATION ON D.S.[1]

Preparation	Pretreatment[2]	Length of Acid Soak, min.	NaOH Conc., %	Reaction Time, hr.
16	Water	10	2.8	4
20	Alcohol	30	3.0	4
21	Alcohol	30	3.0	4
23	Alcohol	30	3.0	4
30	Alcohol	30	0.3	1
31	Benzene	30	0.3	3/4

[1]Results are presented in Figure 1. Nonrandomized rag pulp was used for all preparations except 16, in which cotton linters were used.

[2]See pages 29 to 31. All samples were water soaked. The pulp was then dried or solvent exchanged and dried from methyl alcohol or benzene as listed in the table.

The data presented in Table VI show that the length of time that a sample is treated with the alcoholic chloroacetic acid solution does not greatly effect the D.S. of the CMC product.

In order to determine the effect of the acid treatment on the viscosity and mercerization of these pulps, the series of samples described in Table VII were prepared. Samples were treated for different lengths of time with three different concentrations of chloroacetic acid. The viscosity of each sample was determined by the method mentioned earlier and the results of two independent determinations are given in Table VII. It is seen that little or no degradation occurred in any of the samples. For further CMC preparations, an acid treatment period of 30 minutes was adopted.

TABLE VI

EFFECT OF LENGTH OF ACID TREATMENT ON D.S.

CMC[1] Preparation	Length of Acid Soak, min.	D.S.	$CH_2ClCOOH$ Conc., %
20	15	0.071	20
	30	0.071	
	60	0.060	
	120	0.064	
21	15	0.019	4
	30	0.014	
	60	0.019	
	120	0.020	

[1]Both preparations were carried out on alcohol-pretreated, nonrandomized rag pulp. The substitution reaction in both cases was carried out at a sodium hydroxide concentration of 3% and a reaction time of four hours.

TABLE VII

EFFECT OF CHLOROACETIC ACID ON PULP VISCOSITY[1]

$CH_2ClCOOH$ Conc., %	Length of Acid Soak, min.	Viscosity, sec. 10/27	Efflux Time, sec. 10/28
20	30	616	642
20	120	606	594
10	30	594	583
10	120	583	628
4	30	599	563
4	120	590	613
0	60	608	604
Untreated	0	601	611
Solvent Blank		71.3	71.3

[1]Alcohol pretreated pulp was used throughout this experiment. The chloroacetic acid was dissolved in 40 cc. of isopropyl alcohol per 5 grams of pulp. At the end of the soak period the samples were water washed to neutrality.

These samples were also analyzed by the method outlined earlier to determine if any mercerization had occurred during the acid treatment. The amount of iodine adsorbed by each of the eight samples was approximately constant (0.20-0.23 equivalents/gram), indicating that there had been no mercerization of the samples during the acid treatment. The D.S. of a similar sample was determined before and after the chloroacetic acid treatment and no change in its D.S. was found (0.002). The acid treatment used in this thesis, therefore, does not degrade, mercerize, or carboxymethylate rag pulp.

STUDY OF SUBSTITUTION VARIABLES

Table VIII outlines CMC preparations in which the effects of the sodium hydroxide concentration and the duration of the substitution reaction on the D.S. of the CMC products were studied. The results are given in Figures

2 and 3. The results presented in Figure 2 indicate that it is possible to obtain a higher D.S. material using lower sodium hydroxide concentrations. This trend exists for both alcohol- and benzene-pretreated pulps and appears to be the strongest when the sodium hydroxide concentration is reduced below 1%. In order to prepare these higher D.S. products, and because less degradation was found to occur when lower sodium hydroxide concentrations were used, a sodium hydroxide concentration of 0.3% was used for further work.

TABLE VIII

EXPERIMENTAL CONDITIONS FOR STUDIES OF THE EFFECT OF NaOH CONCENTRATION AND REACTION TIME ON D.S.[1]

CMC Preparation	Pretreatment[2]	$CH_2ClCOOH$ Conc., %	Length of Acid Soak, min.	Reaction Time, hr.	NaOH Conc., %
18	Water	30.0	30	4	1.25-35
27A	Alcohol	5.0	30	4	0.3-3.0
27B	Benzene	5.0	30	4	0.3-3.0
28A	Alcohol	5.0	30	4	0.3-3.0
28B	Benzene	2.0	30	4	0.3-3.0
14 & 15	Water	18.8	7	0.25-2	2.6
22	Alcohol	10.0	30	0.5-7	3.0
29A	Alcohol	5.0	30	0.25-4	0.3
29B	Benzene	2.0	30	0.25-4	0.3

[1]Results are presented in Figures 2 and 3.

[2]See pages 29 to 31. All samples were water soaked. The pulp was then dried or solvent exchanged and dried from methyl alcohol or benzene as listed in the table.

The results of CMC preparations 22 and 29 (Figure 3) indicate that the substitution reaction was essentially completed after the first hour of reaction and that further refluxing caused only a much slower continued

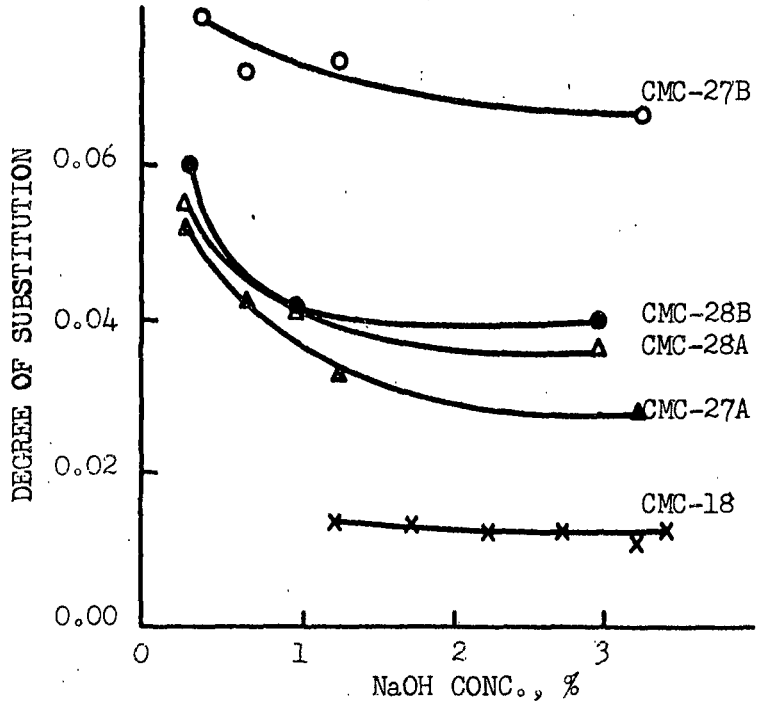

Fig. 2 Effect of Excess NaOH Concentration on Degree of Substitution

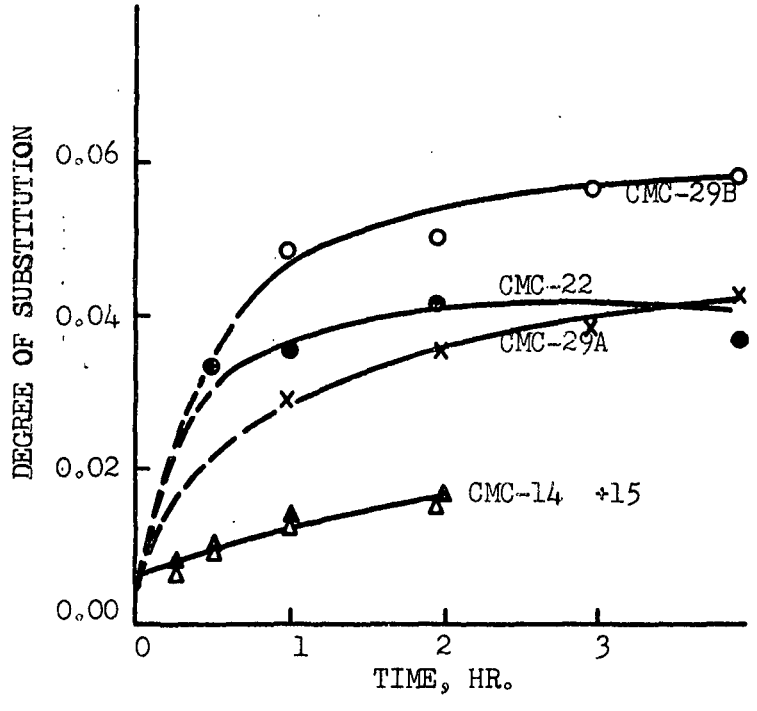

Fig. 3 Effect of Reaction Time on Degree of Substitution

substitution. A reaction time of 45 to 60 minutes was used for the remaining CMC preparations.

In order to determine the effect of the substitution reaction on the viscosity and mercerization of the rag pulp, samples were prepared that had received only the treatment outlined in the substitution and wash procedures (i.e., no acid treatment). The results of viscosity and mercerization determination on these samples are given in Table IX.

TABLE IX

EFFECT OF ALCOHOLIC ALKALI ON PULP VISCOSITY AND MERCERIZATION[1]

NaOH Conc., %	Reaction Time, hr.	Efflux Time, sec.	Iodine Adsorbed, eq./g.
8.0	4	394	0.61
3.0	7	358	0.57
0.0	4	514	0.54
0.0	7	505	0.53

[1]Treatment carried out in a manner similar to the substitution reaction and wash used in CMC preparation. Alcohol-pretreated pulp was used.

It is seen that the iodine adsorption of the pulp had been increased slightly by the alcoholic alkali treatment. This increase was 0.04 to 0.08 equivalents/gram, while the difference between a mercerized and an unmercerized sample, run simultaneously with these samples, was 0.30 equivalent/gram. For the samples given in Table IX this increase in iodine adsorption may be due to slight mercerization or may be due to other effects of the alkali treatment. Since the treated samples did not have

the appearance of mercerized pulps and since the increase in iodine adsorption was considerably less than the increase that occurred with complete mercerization, it was assumed that there was little or no mercerization. The reason for desiring unmercerized CMC samples for this study was to avoid the adverse effects of mercerization on the papermaking properties of pulps reported by Probst (47). Later in this thesis some of the papermaking properties of CMC pulps were determined and were found to have improved over the starting material. This is an indication that the adverse effects on the papermaking behavior of the pulps had been avoided and that the CMC pulps prepared in this study had not been mercerized.

Table IX also presents data on the viscosities of pulps that were treated with alcoholic alkali. It is seen that the alcoholic alkali treatment degrades the pulp. Similar results were obtained several times in this study. Attempts to reduce the amount of degradation by carrying out the substitution reaction in a nitrogen atmosphere or by adding small amounts of reducing agent to the reaction mixture were unsuccessful. In every case the pulp sample was degraded from an initial viscosity of 500 to 600 seconds (D.P. of about 1900) for the control samples to a final viscosity of 300 to 400 seconds (D.P. of about 1500) for the treated pulps. These values were obtained when viscosities were determined on either CMC pulp or pulp that had been treated with alcoholic sodium hydroxide but not substituted.

Table X shows the results of two studies to determine the effect of the sodium hydroxide concentration used in the substitution reaction on the viscosity of the resulting pulps. In both experiments degradation tends to

to be less at the lower caustic concentrations. The choice of a low sodium hydroxide concentration (0.3%) for the remaining CMC preparations was based on the lower degradation obtained in these experiments and the higher D.S.'s obtained when low-caustic concentrations were used in CMC preparations mentioned earlier.

These experiments have resulted in the choice of a 0.3% sodium hydroxide concentration and a reaction time of one hour for other CMC preparations. By using these conditions, D.S.'s up to 0.070 were obtained without mercerization and with a minimum of degradation.

STUDY OF WASHING VARIABLES

The procedure used to neutralize and wash the CMC pulps after the substitution reaction was also studied in this thesis. In two CMC preparations (24 and 25) pulps were prepared according to the procedures outlined earlier except the washing procedure was varied. In these washes dilute aqueous acetic acid and dilute alcoholic hydrochloric acid were used to neutralize separate pulp samples at room temperature and with ice added to the neutralization mixture. Acetic acid neutralizations were carried out before and after the pulp had been water washed, and in both cases the sample was washed with distilled water after the neutralization. After alcoholic hydrochloric acid was used to neutralize two samples, one was extensively water washed and the other was washed with 70% methyl alcohol. The D.S.'s of the CMC samples that had been neutralized and washed by these various methods were determined. There were only slight irregular variations in the D.S. values obtained (0.024-0.035).

TABLE X

EFFECT OF NaOH ON VISCOSITY OF CMC PULPS

	NaOH Conc., %	Efflux Time, sec.	D.S.
CMC preparation 28A[1]	3.0	389	0.036
	1.0	455	0.041
	0.3	500	0.055
CMC preparation 28B[1]	3.0	257	0.039
	1.0	227	0.041
	0.3	409	0.060
Alkali treatment[2]	3.0	469	
	1.0	527	
	0.3	563	
	0.1	562	

[1]Treatment of CMC preparations 28 A and B is given in Table VIII.

[2]Treatment carried out in a manner similar to the substitution reaction and wash used in CMC preparations. Benzene pretreated pulp and a reaction time of one hour were used.

A similar series of experiments were carried out to determine the effect of the various neutralization and washing methods on the viscosities of the resulting pulps. No major differences in viscosity were observed (η_{rel} = 5.0 to 5.8).

The various neutralization and wash procedures studied all appear to have a similar effect on the D.S. and the viscosity of resulting CMC pulps. The procedure of neutralization with aqueous acetic acid and washing with distilled or deionized water was used for many of the CMC preparations because it is a procedure that was easily duplicated for each of the CMC preparations.

FINAL CMC PREPARATIONS

The preceding paragraphs have described studies of the variables in each stage of CMC preparation. The method of CMC preparation that has been developed is fairly reproducible between runs, and low-D.S. CMC pulps have been prepared without mercerization and without excessive degradation. These preparations, however, have been carried out in most instances on 5-gram samples. It was now desired to produce similar low-D.S. CMC pulps in larger amounts in order to determine some of their papermaking properties. In order to obtain an idea of the range of D.S. to be studied and to devise a workable method of preparing larger amounts of CMC pulps, two preliminary CMC preparations (34 and 35) were carried out.

CMC preparation 34 was the initial attempt to prepare 700 grams of a CMC pulp. The procedures used have been presented in an earlier section

and are essentially the same as were used in the preparation of 5-gram samples except that proportionately larger amounts of reagents and larger equipment were used. In this preparation a chloroacetic acid concentration of 2.0% was used and a D.S. of 0.048 was obtained. Besides being the initial attempt to prepare larger amounts of CMC, the pulp from this preparation was also used to determine the difference between the papermaking properties of the acid form and the sodium salt form of CMC. The pulp sample was divided in half after the acetic acid neutralization of the reaction mixture. Half of the pulp was carried through the bicarbonate soak and water wash outlined in a previous section (page 32) in order to form the sodium salt of the CMC (sample 34B). The bicarbonate soak was omitted from the treatment of the other half of the pulp and the wash was completed with distilled water in order to retain the acid form of the CMC (sample 34A). Some of the properties of these two samples are given in Table XXI and are discussed in the next section of this thesis. The sodium salt form of CMC was chosen for further study because of its superior properties observed in this experiment.

CMC preparation 35 was designed to determine what D.S. range should be investigated in the final series of CMC preparations. Five samples of 100 grams of pulp each were prepared including two control samples and three CMC samples. One of the two control samples was an untreated sample of standard rag pulp and the other sample was treated in a manner exactly similar to the CMC samples except that the chloroacetic acid was omitted from the acid treatment and thus no substitution occurred. The three CMC samples had D.S.'s of 0.019, 0.047, and 0.066. Some of the papermaking properties of these pulps were determined according to methods outlined in a following section. The results of these

determinations are not included in this thesis since the study was exactly duplicated on a larger scale in CMC preparations 36 to 43. The CMC sample of D.S. equal to 0.066 is of interest however. This sample was slimy to the touch and filtered very slowly, making the wash procedure very long and difficult. After preparing this sample it was felt that CMC samples of higher D.S.'s would be extremely hard to handle and should not be included in this study.

CMC preparations 36 to 43 were the final eight preparations carried out for this thesis. A 700-gram sample, enough for a study of papermaking properties, was prepared in each case. These eight samples include two control pulps and six CMC pulps in the D.S. range 0.006 to 0.062. The method of preparing the CMC pulps was given in an earlier section (pages 29 to 33). The chloroacetic acid concentrations used and the D.S.'s obtained for each preparation are given in Table XI and Figure 4.

TABLE XI

FINAL CMC PREPARATIONS

CMC Preparation	$CH_2ClCOOH$ Conc., %	D.S.	Intrinsic Viscosity	D.P.
36-F	0.00	0.002	11.5	1960
37-G	0.00	0.002	5.6	950
42-H	0.10	0.006	6.3	1070
40-J	0.25	0.014	7.7	1310
38-K	0.50	0.022	5.5	940
41-L	1.00	0.036	7.0	1190
43-M	1.50	0.053	6.6	1120
39-N	2.00	0.062	6.6	1120

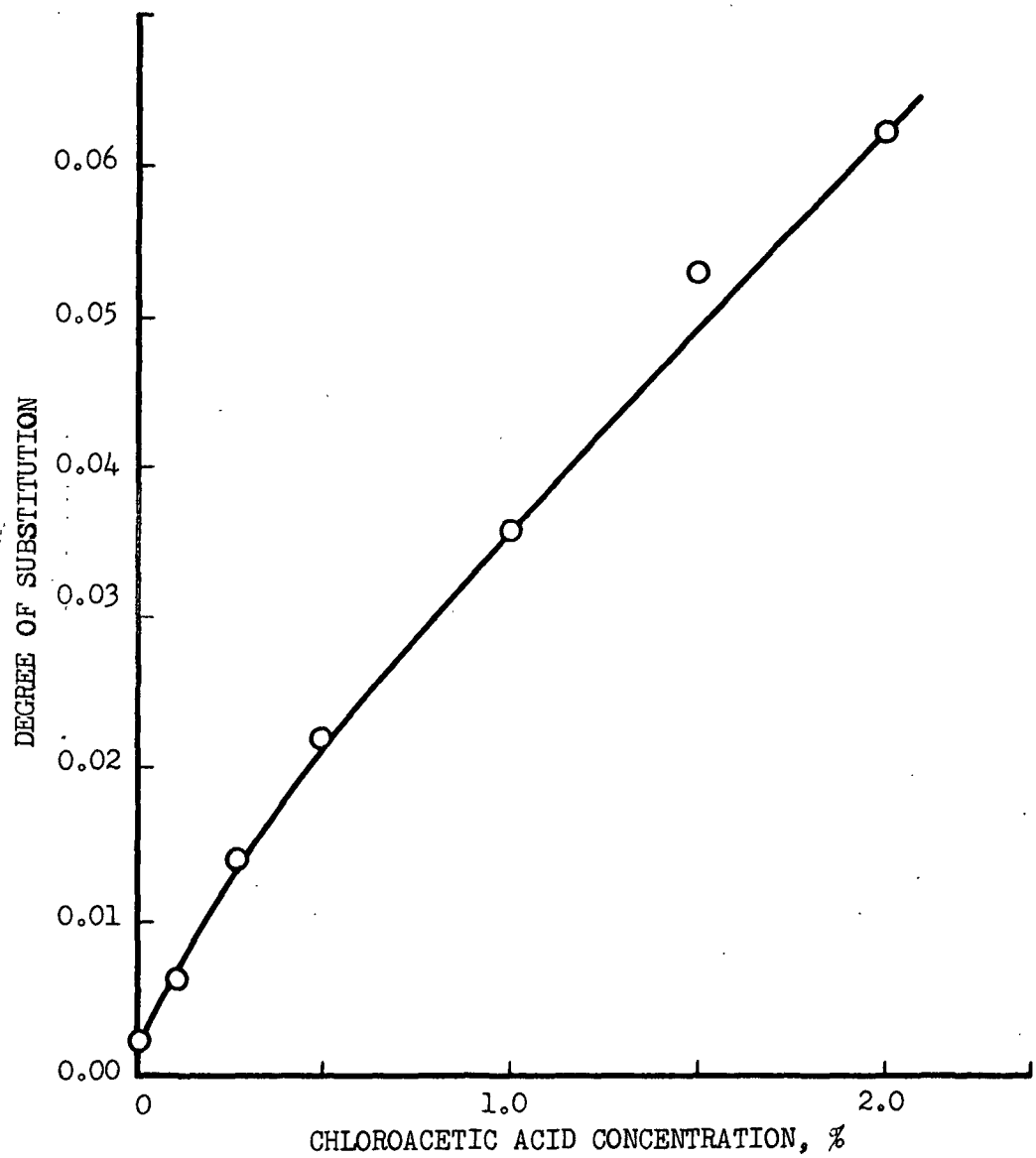

Fig. 4 Degree of Substitution Obtained at the Various Chloroacetic Acid Concentrations

Control pulp 36F is the untreated control sample for this series of experiments. For this sample the pretreatment was carried only through the defibration stage. Instead of the usual solvent exchange the defibrated pulp was thickened on a Buchner funnel and placed in a Pliofilm bag in the cold room until its beater run was made.

Control pulp 37G is the treated control pulp for this series of experiments. It was treated exactly as the CMC pulps except that the chloroacetic acid was omitted from the acid-treatment procedure.

The numbers (36 to 43) assigned to the pulps from these final CMC preparations indicate their order of preparation. The letters (F to N) were assigned to these pulps in the order of their D.S. The two control pulps (D.S.'s of 0.002) are samples F and G; pulp H has a D.S. of 0.006, and pulp J has a D.S. of 0.014, etc., up to pulp sample N which has a D.S. of 0.062.

Figure 4 shows the nearly linear dependence of the D.S. obtained on the concentration of the chloroacetic acid used in a given preparation. This figure also shows the range of D.S. studied and the location of each sample in this range. It is seen that there are more samples in the lower D.S. range where, as will be shown in later graphs, the pulp properties change rapidly with D.S.

In order to determine if the D.S. value of a pulp changed significantly during the beating and handsheet formation operations described in a following section, a D.S. determination was carried out on handsheet scraps from CMC preparation 39 N. These scraps were redispersed in water, soaked in dilute acetic acid overnight, and thoroughly water washed before their D.S. was

determined. This procedure gave a D.S. value of 0.058 versus a D.S. of 0.062 obtained on the original pulp. Since this experiment was carried out on the highest D.S. sample it may be concluded that the D.S. values in this study change only slightly with beating and sheetmaking.

Figure 5 is a semilog plot of reduced viscosity versus concentration to determine the intrinsic viscosity and consequently the D.P. of each of the CMC samples. The procedure involved in obtaining these viscosities was discussed earlier in this thesis (page 20). The plots of samples L, M, and H have been omitted from this graph in order to simplify it. If shown on this figure, these plots would lie between lines J and G. The intrinsic viscosities derived from this graph and the corresponding degrees of polymerization are given in Table XI.

In these CMC preparations and in the preparation of the untreated control pulp G, the D.P. of about 2000 of the original rag pulp was lowered to a D.P. in the range of 900 to 1300. It was shown in earlier experiments that this degradation occurs during the substitution procedure when the pulp is treated with boiling alcoholic sodium hydroxide.

In Figure 5 the curve for preparation N is of special interest. For this sample (the highest D.S. pulp) viscosities were obtained at seven different concentrations to determine if the straight line relationship between the concentration and the log of the reduced viscosity held for these low-D.S. CMC pulps. It is seen from Figure 5 that the points fall on a straight line down to a concentration of 0.05 grams per 100 cc. Below this concentration the points fall below the line. This drop off of the curve at low concentrations may be due to cross linking according to Batzer and co-workers (48). The points above 0.05 grams per 100 cc. for this and

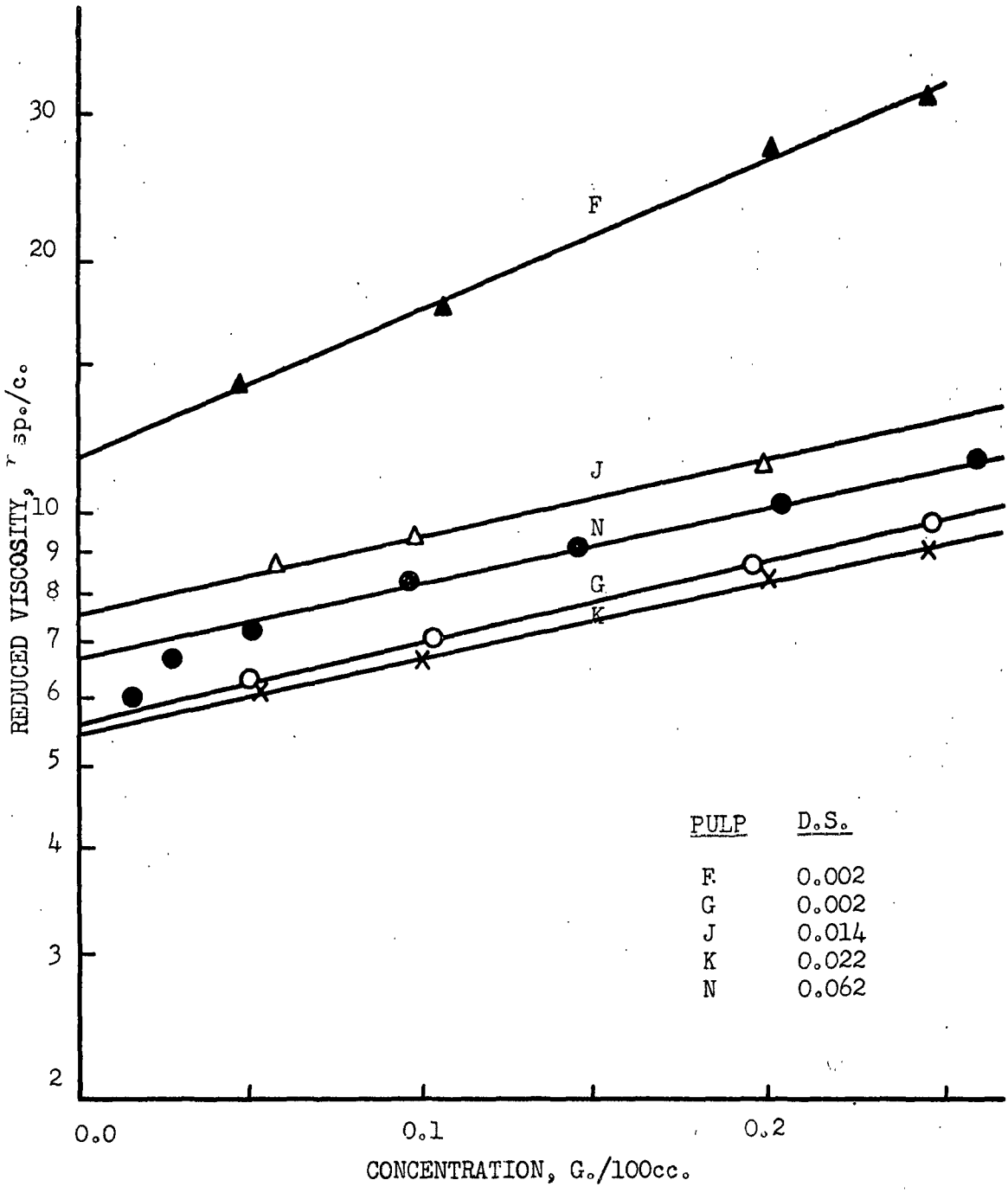

Fig. 5 Reduced Viscosity versus Concentration to Determine Intrinsic Viscosity

the other samples fall on a straight line. This may be taken as evidence to support the assumption made earlier that the electrolytic nature of the carboxymethyl group does not appreciably affect the measured viscosity, due to the low D.S.'s of the pulps.

Two control pulps have been included in this series of pulps. The untreated control pulp (F) gives a base line to this study, as its properties are those available if the treatment outlined in this report is not undertaken. Sample G, the treated control pulp of this series, is also uncarboxymethylated but its degree of polymerization is in the same range as the CMC pulps. These two control pulps permit the differentiation of the changes in properties that are due to carboxymethylation and those changes that are due to the other treatments and handling necessary to carboxymethylate a pulp in this study.

This section has presented a fairly complete study of one method of preparing CMC, starting with the initial attempts to devise a suitable method, through a study of the variables involved in this method, and ending with the preparation, by the resulting method, of a series of CMC pulps with D.S.'s from 0.006 to 0.062 in sufficient quantities to permit a further study of their papermaking properties. The method of preparation devised involves the use of an isopropyl alcohol reaction medium and very low concentrations of chloroacetic acid and sodium hydroxide in order to obtain substitution without mercerization and with a minimum of degradation. The goal of this thesis to study and develop a reproducible method of preparing low-D.S. CMC pulps, retaining the fibrous nature of the original cellulose pulps and without excessive degradation or mercerization has been achieved. It remains to determine some of the papermaking properties of these pulps.

PAPERMAKING PROPERTIES OF CMC PULPS

BEATER RUN AND HANDSHEET TESTING PROCEDURES

Of the several laboratory devices available for strength evaluation of pulps, the Jokro mill was chosen for use in this study. The chief reasons for this choice are:

1. The Jokro mill requires only about 100 grams of pulp for a complete six point beater run, including moisture determination, freeness, and five handsheets per beater interval.
2. The Jokro mill permits the simultaneous beating of six different stocks.
3. Results obtained with the Jokro mill have been found to be reproducible between pots and between runs (49).
4. Results obtained with the Jokro mill are similar to results obtained using the Valley Beater (49).

As was mentioned earlier, the prepared pulps were stored in the cold room in polyethylene bags. The consistencies of these pulps were determined by Institute Method 413. Samples corresponding to 16 grams of ovendry pulp were weighed out, placed in each Jokro mill pot, and diluted to 6% consistency. The Jokro mill was run according to the manufacturer's instructions. At the end of a beater interval the beaten pulp was washed into a British disintegrator pot and diluted to 2 liters. The pulp was then given 7500 revolutions in the disintegrator and washed into a stainless steel bucked with 1 liter of water.

Except in Preparation 34 duplicate Jokro pots were run for each beater interval in order to obtain 32 grams of beaten pulp per beater interval. The pulps from the two pots were combined after treatment in the British disintegrator.

In each beater run six beater intervals were obtained, from the initial unbeaten pulp to a final freeness of about 300 cc. Schopper-Riegler.

Schopper-Riegler freeness and Bauer-McNett fiber classifications were run on the pulp from each beater interval according to Institute Methods 414 and 415.

From 10 to 14 handsheets were made and tested at each beater interval according to Institute Method 411. The following tests were carried out on these handsheets after they had been conditioned to 73 ± 3°F. and 50 ± 2% relative humidity.

TABLE XII

HANDSHEET TESTING METHODS

Tests	Institute Method
Basis weight	504
Density and caliper	508
Burst	510
Tensile-stretch	511
Tear	512
MIT fold	513
Porosity	514
Opacity	524
Moisture	611
Taber stiffness	530

One additional test was run. The zero-span tensile strengths of the sheets were determined according to Institute Method 527 using a set of jaws of more recent design (50). A clamping load of 350 to 400 pounds was used.

EXPERIMENTAL RESULTS

The papermaking properties of the pulps from CMC preparations 34, and 36 to 43 were determined by the experimental methods outlined previously. The data obtained from this study are presented in Tables XIII to XXI. In this section a series of graphs and photomicrographs are also presented to show the changes in properties that have occurred due to carboxymethylation. A brief discussion of each of these graphs is included to point out these changes.

EASE OF BEATING

Figure 6 is a plot of the pulp freeness versus the beating time in the Jokro mill for all eight samples that were prepared and tested. It is seen from this figure that as the D.S. of a pulp is increased, the pulp can be beaten to a given freeness more easily.

This increase in ease of beating is due to at least two different effects. The difference between the two control pulps (F and G) shows that part of the increase in ease of beating is due to other effects of the preparation besides carboxymethylation. The alkali cook with its consequent degradation of the pulp is probably the chief factor in this change in ease of beating. The various CMC pulps show a further increase in ease of beating and this increase is dependent on the D.S. (i.e., with the exception of sample H the ease of beating increases with increasing D.S.).

The relationship between pulp freeness and the apparent density of the handsheets is almost linear over the range of freeness encountered in this study. A comparison of samples at a given freeness, therefore, is approximately equivalent to a comparison of the same samples at a given apparent density.

TABLE XIII

PULP AND HANDSHEET PROPERTIES OF PREPARATION 36-F, D.S. = 0.002

Beating time, min.	0	10	25	40	55	70	85
PULP PROPERTIES							
S.-R. freeness, cc.	795	710	575	480	420	375	320
Fiber classification, Fiber retained, %							
on 20-mesh	55.3	48.0	25.7	21.6	12.8	7.3	4.3
thru 20- on 35-mesh	25.0	28.6	39.2	41.7	41.6	45.8	44.4
thru 35- on 65-mesh	5.4	7.7	9.5	11.2	13.5	14.2	15.7
thru 65- on 150-mesh	3.5	5.3	6.8	8.1	10.3	11.0	12.4
thru 150-mesh	10.8	10.4	18.8	17.4	21.8	21.7	23.2
HANDSHEET PROPERTIES							
Basis weight, 25x40x500, lb.	44.2	46.3	45.3	44.8	44.4	45.3	45.6
Caliper, mils	4.86	4.14	3.71	3.53	3.43	3.39	3.30
Apparent density	9.1	11.2	12.2	12.7	12.9	13.3	13.8
Burst, pt./100 lb.	25.8	49.7	60.6	64.9	60.5	62.8	64.2
Tensile, lb./in.	6.2	13.7	16.4	17.5	17.8	18.5	18.8
Stretch, %	3.1	5.5	5.1	5.1	5.1	4.8	4.4
Tear factor	2.89	3.17	2.47	2.20	1.87	1.83	1.76
M.I.T. fold	7	42	74	70	61	58	91
Porosity, sec./100 cc.	3	19	53	102	153	227	378
TAPPI opacity	81.5	77.5	76.0	75.0	75.5	75.5	76.0
Taber stiffness	1.70	1.77	1.72	1.55	1.53	1.57	1.53
Zero-span tensile, lb./in.	40.0	43.7	45.8	46.5	46.7	45.8	44.9
Equilibrium moisture, 73°F., 50% R.H.	6.4	6.4	6.4	6.4	6.5	6.5	6.5

TABLE XIV

PULP AND HANDSHEET PROPERTIES OF PREPARATION 37-G, D.S. = 0.002

Beating time, min.	0	10	20	30	40	50
PULP PROPERTIES						
S.-R. freeness, cc.	810	635	510	420	345	305
Fiber classification,						
Fiber retained, %						
on 20-mesh	70.9	54.0	35.2	22.7	13.2	7.4
thru 20- on 35-mesh	12.9	22.3	35.4	41.8	44.5	41.5
thru 35- on 65-mesh	5.8	8.5	10.9	13.8	15.0	18.4
thru 65- on 150-mesh	3.3	5.8	7.7	10.3	11.7	15.7
thru 150-mesh	7.1	9.4	10.8	11.4	15.6	17.0
HANDSHEET PROPERTIES						
Basis weight,						
25x40x500, lb.	47.0	46.2	46.1	45.6	45.7	46.2
Caliper, mils	5.24	4.05	3.80	3.61	3.51	3.43
Apparent density	9.0	11.4	12.1	12.6	13.0	13.4
Burst, pt./100 lb.	25.8	53.6	57.5	57.1	61.3	59.7
Tensile, lb./in.	6.5	15.1	16.9	16.8	18.4	19.0
Stretch, %	4.1	5.8	5.5	4.8	5.5	4.8
Tear factor	2.79	2.49	2.02	1.82	1.75	1.45
M.I.T. fold	6	47	44	41	58	48
Porosity, sec./100 cc.	3	25	55	67	137	192
TAPPI opacity	82.5	79.0	77.5	76.0	74.5	74.5
Taber stiffness	1.77	1.68	1.70	1.60	1.61	1.70
Zero-span tensile,						
lb./in.	42.2	45.5	44.7	42.8	45.3	45.9
Equilibrium moisture,						
73°F., 50% R.H.	6.2	6.3	6.3	6.4	6.4	6.4

TABLE XV

PULP AND HANDSHEET PROPERTIES OF PREPARATION 42-H, D.S. = 0.006

Beating time, min.	0	11	15	20	25	30
PULP PROPERTIES						
S.-R. freeness, cc.	780	510	430	350	310	250
Fiber classification, Fiber retained, %						
on 20-mesh	70.2	50.9	46.0	36.6	34.8	18.0
thru 20- on 35-mesh	11.8	23.6	24.0	28.8	28.1	38.1
thru 35- on 65-mesh	5.3	8.4	9.9	11.0	12.7	13.6
thru 65- on 150-mesh	3.9	6.8	8.2	9.2	10.8	12.1
thru 150-mesh	8.8	10.3	11.9	14.4	13.6	18.2
HANDSHEET PROPERTIES						
Basis weight, 25x40x500, lb.	44.0	44.3	45.9	45.5	45.6	46.2
Caliper, mils	4.40	3.59	3.58	3.51	3.40	3.41
Apparent density	10.0	12.3	12.5	12.9	13.4	13.5
Burst, pt./100 lb.	29.5	68.2	70.4	74.9	75.7	81.4
Tensile, lb./in.	6.9	17.1	18.8	19.1	20.4	21.7
Stretch, %	3.8	5.8	6.1	5.5	5.8	5.8
Tear factor	2.69	2.17	2.09	1.89	1.88	1.64
M.I.T. fold	8	93	106	135	137	191
Porosity, sec./100 cc.	3	43	69	99	156	216
TAPPI opacity	77.5	74.0	73.5	72.5	70.0	71.0
Taber stiffness	1.30	1.47	1.58	1.67	1.56	1.75
Zero-span tensile, lb./in.	38.1	42.3	46.0	47.3	48.3	48.0
Equilibrium moisture, 73°F., 50% R.H.	6.5	6.6	6.7	6.7	6.5	6.6

TABLE XVI

PULP AND HANDSHEET PROPERTIES OF PREPARATION 40-J, D.S. = 0.014

Beating time, min.	0	10	20	25	31	38
PULP PROPERTIES						
S.-R. freeness, cc.	760	540	400	340	310	250
Fiber classification, Fiber retained, %						
on 20-mesh	65.4	46.8	45.4	30.9	23.7	18.1
thru 20- on 35-mesh	9.8	27.0	24.0	37.0	39.2	43.7
thru 35- on 65-mesh	5.9	7.5	9.1	9.9	10.9	12.4
thru 65- on 150-mesh	3.3	5.0	6.4	7.4	7.8	9.4
thru 150-mesh	15.6	13.7	15.1	14.7	18.4	16.4
HANDSHEET PROPERTIES						
Basis weight, 25x40x500, lb.	44.6	46.0	45.1	45.4	45.6	46.2
Caliper, mils	4.78	3.79	3.52	3.45	3.40	3.37
Apparent density	9.33	12.1	12.7	13.1	13.4	13.7
Burst, pt./100 lb.	35.2	80.5	95.4	99.1	99.0	102
Tensile, lb./in.	8.1	19.8	24.1	24.6	25.6	25.1
Stretch, %	4.1	6.1	6.1	6.5	6.5	6.1
Tear factor	3.01	2.50	1.99	1.98	1.89	1.73
M.I.T. fold	13	166	472	485	549	599
Porosity, sec./100 cc.	3	45	108	178	259	339
TAPPI opacity	79.0	73.0	70.5	69.5	69.5	70.0
Taber stiffness	1.38	1.58	1.68	1.70	1.65	1.95
Zero-span tensile, lb./in.	37.2	47.7	50.8	52.0	52.1	51.8
Equilibrium moisture, 73°F., 50% R.H.	6.7	6.7	6.8	6.8	6.8	6.8

TABLE XVII

PULP AND HANDSHEET PROPERTIES OF PREPARATION 38-K, D.S. = 0.022

Beating time, min.	0	5	10	15	21	27
PULP PROPERTIES						
S.-R. freeness, cc.	760	570	460	405	325	275
Fiber classification, Fiber retained, %						
on 20-mesh	63.6	54.6	44.4	32.1	21.6	15.5
thru 20- on 35-mesh	16.6	24.7	30.8	41.4	51.1	51.2
thru 35- on 65-mesh	5.5	7.1	7.7	9.0	10.0	11.1
thru 65- on 150-mesh	2.9	3.9	4.5	5.3	6.4	7.7
thru 150-mesh	11.4	9.7	12.6	12.2	10.9	14.5
HANDSHEET PROPERTIES						
Basis weight, 25x40x500, lb.	46.2	46.2	45.4	46.3	46.5	46.0
Caliper, mils	4.68	3.84	3.60	3.59	3.49	3.37
Apparent density	9.86	12.0	12.6	12.9	13.3	13.9
Burst, pt./100 lb.	39.9	80.5	95.0	97.4	102	108
Tensile, lb./in.	9.2	19.6	22.7	24.2	25.4	27.1
Stretch, %	4.8	6.5	7.2	6.5	6.5	7.2
Tear factor	2.91	2.50	2.07	1.95	1.85	1.78
M.I.T. fold	19	225	488	523	643	786
Porosity, sec./100 cc.	4	31	64	100	182	351
TAPPI opacity	79.5	73.0	69.5	69.5	60.0	67.0
Taber stiffness	1.60	1.70	1.70	1.73	1.83	1.63
Zero-span tensile, lb./in.	42.7	45.6	46.3	48.6	49.0	48.6
Equilibrium moisture, 73°F., 50% R.S.	6.6	6.8	6.7	6.9	6.9	6.9

TABLE XVIII

PULP AND HANDSHEET PROPERTIES OF PREPARATION 41-L, D.S. = 0.036

Beating time, min.	0	4	8	12	18	24
PULP PROPERTIES						
S.-R. freeness, cc.	715	580	460	405	320	260
Fiber classification, Fiber retained, %						
on 20-mesh	59.1	57.4	51.8	41.4	39.9	29.0
thru 20- on 35-mesh	18.2	21.4	23.2	32.6	31.4	38.6
thru 35- on 65-mesh	6.2	7.1	7.0	7.2	8.9	9.4
thru 65- on 150-mesh	3.3	4.1	4.0	4.4	6.0	6.5
thru 150-mesh	13.2	10.0	14.0	14.4	13.8	16.5
HANDSHEET PROPERTIES						
Basis weight, 25x40x500, lb.	45.1	45.5	45.2	45.6	45.6	45.3
Caliper, mils	4.61	3.86	3.63	3.55	3.38	3.33
Apparent density	9.8	11.8	12.4	12.8	13.5	13.6
Burst, pt./100 lb.	51.5	95.5	108	118	122	135
Tensile, lb./in.	11.2	21.7	23.9	24.4	27.9	29.3
Stretch, %	7.2	7.5	7.5	6.5	7.5	7.2
Tear factor	3.13	2.66	2.55	2.04	1.82	1.63
M.I.T. fold	30	421	652	1013	697	1302
Porosity, sec./100 cc.	4	27	44	95	370	620
TAPPI opacity	77.5	77.0	69.5	67.5	66.5	66.5
Taber stiffness	1.52	1.75	1.68	1.72	1.53	1.52
Zero-span tensile, lb./in.	42.8	48.2	47.8	50.1	48.8	52.3
Equilibrium moisture, 73°F., 50% R.H.	7.1	7.2	7.3	7.3	7.3	7.3

TABLE XIX

PULP AND HANDSHEET PROPERTIES OF PREPARATION 43-M, D.S. = 0.053

Beating time, min.	0	4	8	12	16	20
PULP PROPERTIES						
S.-R. freeness, cc.	680	520	440	370	300	265
Fiber classification,						
Fiber retained, %						
on 20-mesh	59.2	48.0	39.0	40.8	32.0	21.1
thru 20- on 35-mesh	16.9	27.1	34.0	27.4	37.3	46.3
thru 35- on 65-mesh	5.6	7.8	8.5	9.2	10.4	11.2
thru 65- on 150-mesh	4.2	4.3	4.6	5.3	6.1	6.1
thru 150-mesh	14.1	12.8	13.9	17.3	14.2	15.3
HANDSHEET PROPERTIES						
Basis weight,						
25x40x500, lb.	44.8	46.6	46.3	46.3	46.8	45.9
Caliper, mils	4.23	3.89	3.64	3.50	3.38	3.25
Apparent density	10.6	12.0	12.7	13.2	13.8	14.1
Burst, pt./100 lb.	75.4	110	121	128	130	135
Tensile, lb./in.	15.2	23.7	26.2	28.4	29.0	27.8
Stretch, %	7.8	7.5	7.5	7.5	7.5	7.8
Tear factor	2.63	2.12	1.86	1.66	1.49	1.46
M.I.T. fold	107	497	546	818	1136	818
Porosity, sec./100 cc.	6	33	89	202	586	890
TAPPI opacity	74.0	69.5	67.5	66.5	65.5	63.5
Taber stiffness	1.72	1.78	1.67	1.63	1.57	1.50
Zero-span tensile,						
lb./in.	43.3	47.3	47.2	49.2	52.7	47.5
Equilibrium moisture,						
73°F., 50% R.H.	7.2	7.4	7.4	7.4	7.5	7.5

TABLE XX

PULP AND HANDSHEET PROPERTIES OF PREPARATION 39-N, D.S. = 0.062

Beating time, min.	0	2	4	6	9	12
PULP PROPERTIES						
S.-R. freeness, cc.	600	490	430	415	330	300
Fiber classification, Fiber retained, %						
on 20-mesh	50.7	47.8	50.5	43.9	38.2	37.9
thru 20- on 35-mesh	31.5	39.7	34.8	38.8	48.3	51.3
thru 35- on 65-mesh	6.4	7.4	6.9	6.7	7.5	7.4
thru 65- on 150-mesh	3.3	3.6	3.8	3.6	3.9	3.0
thru 150-mesh	8.1	1.5	4.0	7.0	2.1	0.4
HANDSHEET PROPERTIES						
Basis weight, 25x40x500, lb.	46.0	47.0	47.0	46.7	46.7	46.1
Caliper, mils	4.27	3.99	3.85	3.75	3.65	3.53
Apparent density	10.8	11.8	12.2	12.5	12.8	13.1
Burst, pt./100 lb.	82.4	104	116	124	135	137
Tensile, lb./in.	17.6	23.7	25.7	26.6	29.0	27.6
Stretch, %	7.8	7.2	7.5	6.8	7.2	7.2
Tear factor	2.44	2.17	1.98	1.93	1.78	1.74
M.I.T. fold	170	424	986	1292	1036	1267
Porosity, sec./100 cc.	7	20	34	60	86	127
TAPPI opacity	73.0	69.5	70.0	67.5	66.5	65.5
Taber stiffness	1.58	1.80	2.00	1.71	1.81	1.90
Zero-span tensile, lb./in.	44.6	47.0	48.2	49.0	50.8	52.8
Equilibrium moisture, 73°F., 50% R.H.	7.4	7.4	7.4	7.5	7.5	7.6

TABLE XXI

PULP AND HANDSHEET PROPERTIES OF PREPARATION 34, D.S. = 0.048

Beating time, min.	0	5.0	7.5	10.0	12.5	15.0
ACID FORM (A)						
S.-R. freeness, cc.	725	545	475	440	430	375
Basis weight, 25x40x500, lb.	45.6	45.9	46.2	46.3	46.4	46.2
Caliper, mils	4.52	3.78	3.74	3.68	3.64	3.58
Apparent density	10.1	12.1	12.3	12.6	12.7	12.9
Burst, pt./100 lb.	56.2	97.0	99.7	103	105	106
Tensile, lb./in.	12.5	23.0	23.3	25.0	25.9	25.2
Tear factor	2.79	2.16	2.01	2.01	1.86	1.74
SODIUM SALT FORM (B)						
S.-R. freeness, cc.	670	510	445	410	380	335
Basis weight, 25x40x500, lb.	43.6	44.5	44.7	44.1	44.0	45.4
Caliper, mils	4.20	3.66	3.62	3.48	3.38	3.48
Apparent density	10.4	12.2	12.4	12.7	13.0	13.1
Burst, pt./100 lb.	69.0	108	116	118	125	124
Tensile, lb./in.	15.1	24.4	26.8	26.1	28.9	28.5
Tear factor	2.78	2.09	2.01	1.95	1.95	1.83

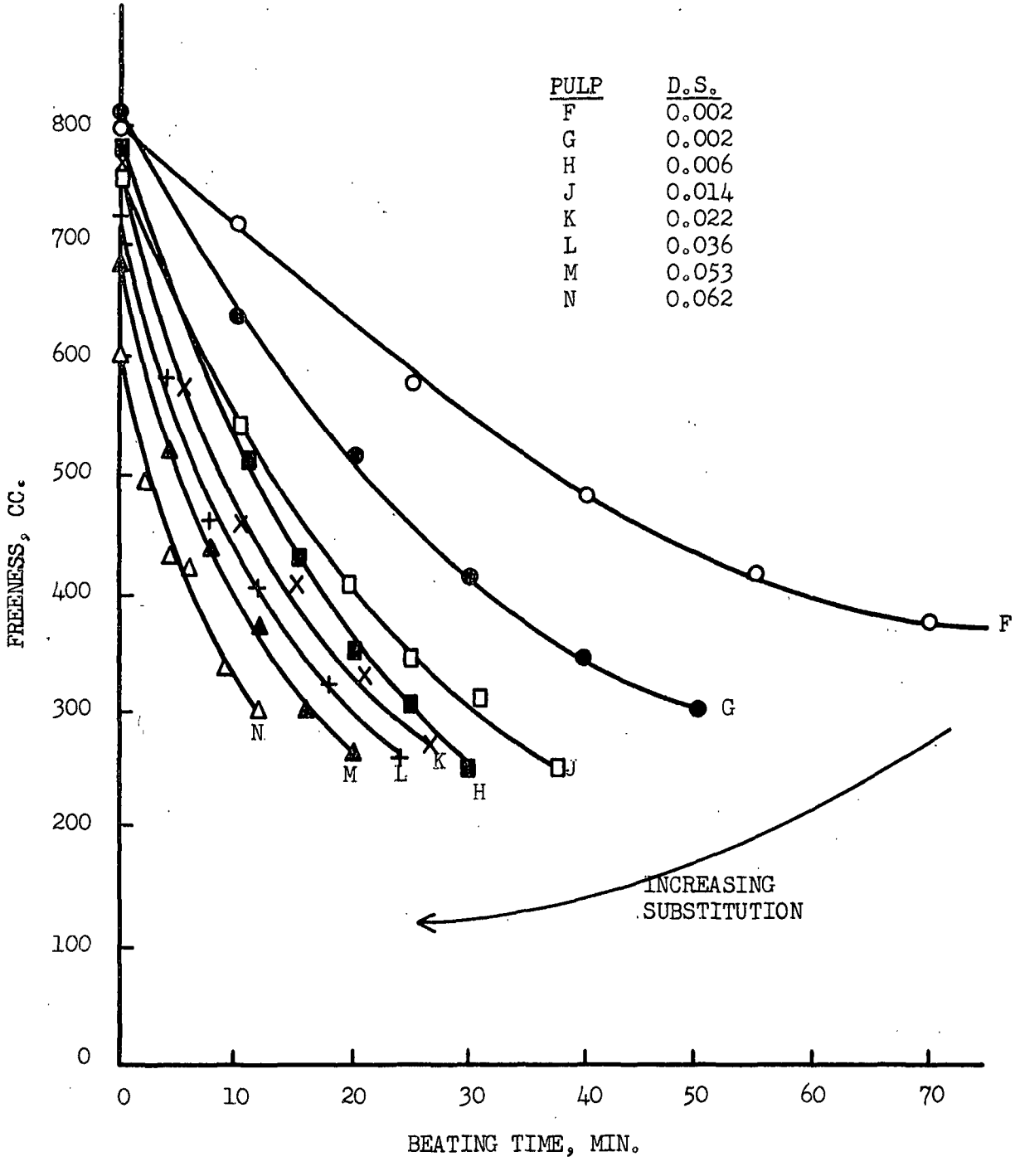

Fig. 6 Freeness versus Beating Time

BURST AND TENSILE

Figures 7 to 10 will be considered together, for they present the burst and tensile data for this study. Figures 7 and 9 present the burst and tensile data as a function of beating time, and Figures 8 and 10 present the change in burst and tensile with D.S. at both constant freeness and the initial or zero beating interval.

A comparison of the points for the two control pulps (F and G) in both Figures 7 and 9 show that there is no substantial difference in their strengths or strength development, i.e., the increase in strength of the CMC sheets is due to carboxymethylation. The maximum burst and tensile values obtained on the higher D.S. sheets are respectively 100 and 60% greater than the maximum values obtained on the control pulps.

The curves in Figures 9 and 10 show that the increase in burst and tensile strengths is the most rapid in the D.S. range up to about 0.030. Above this D.S. the strengths of handsheets from CMC pulps level off or increase only gradually with a continued increase in D.S. An exception to this is preparation N (D.S. = 0.062). In this case, at 500 and 600 cc. Schopper-Riegler freeness, the burst and tensile values are lower than at the preceding two points of lower D.S.'s. The points at 300 and 400 cc. Schopper-Riegler freeness, however, seem to be in line for this preparation.

The burst and tensile strengths of handsheets made from unbeaten pulp for each preparation are also plotted on Figures 8 and 10. It is seen that the strength of these sheets increases with D.S. until, in the case of burst, it exceeds the maximum value obtained with the control pulps; and in the case of tensile, it almost equals the maximum values obtained by

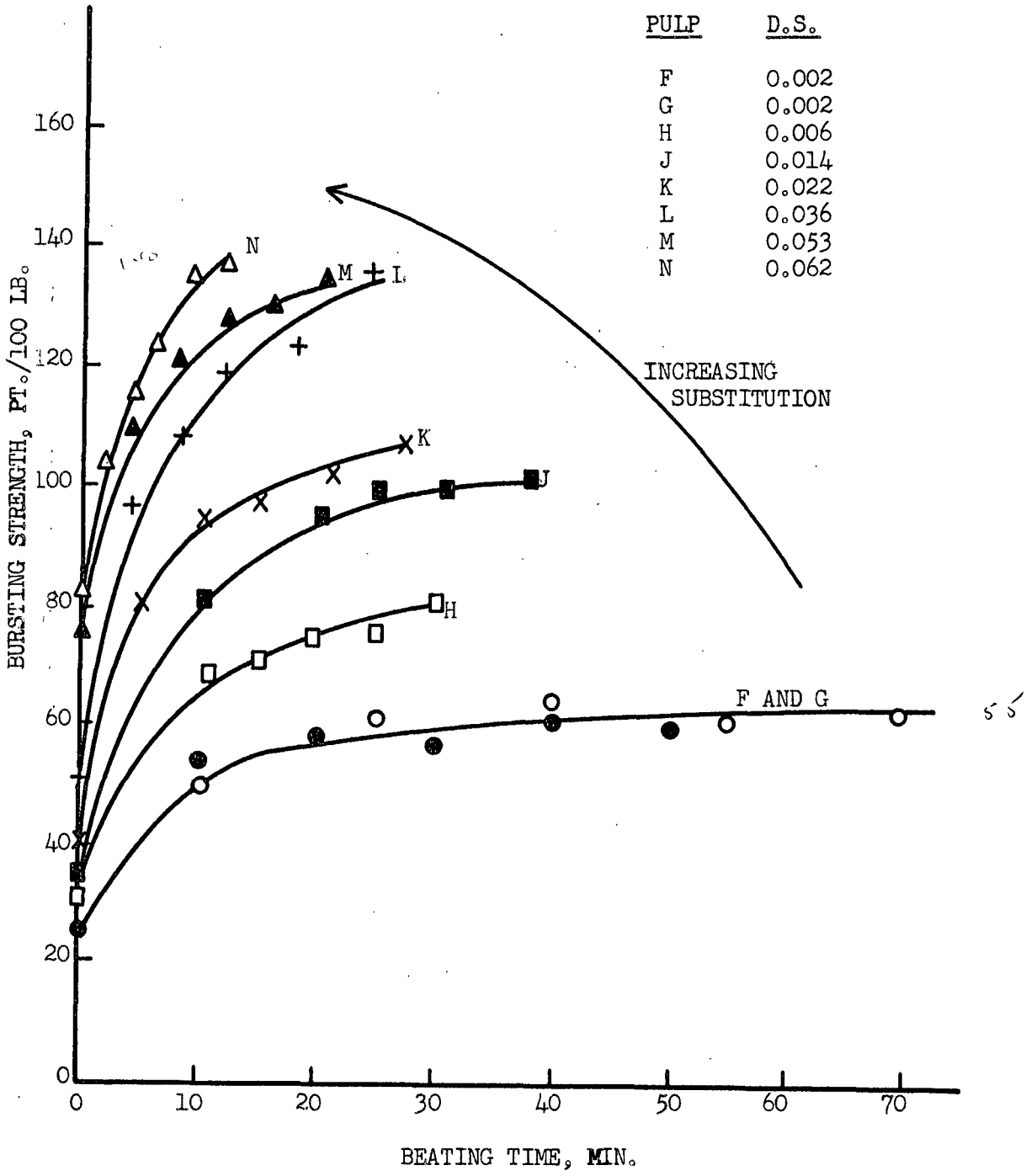

Fig. 7 Bursting Strength versus Beating Time

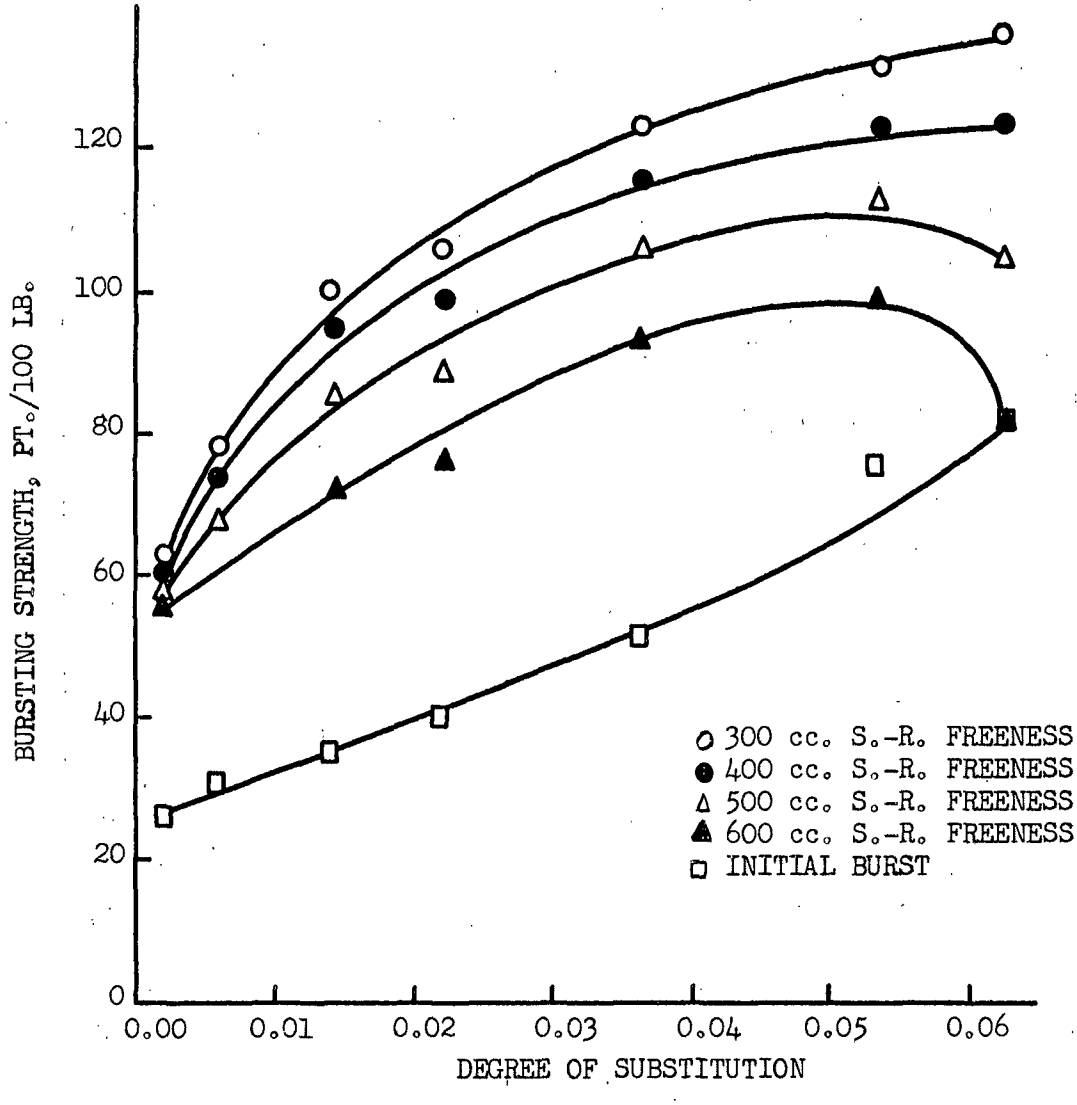

Fig. 8 Bursting Strength versus Degree of Substitution at Constant Freeness

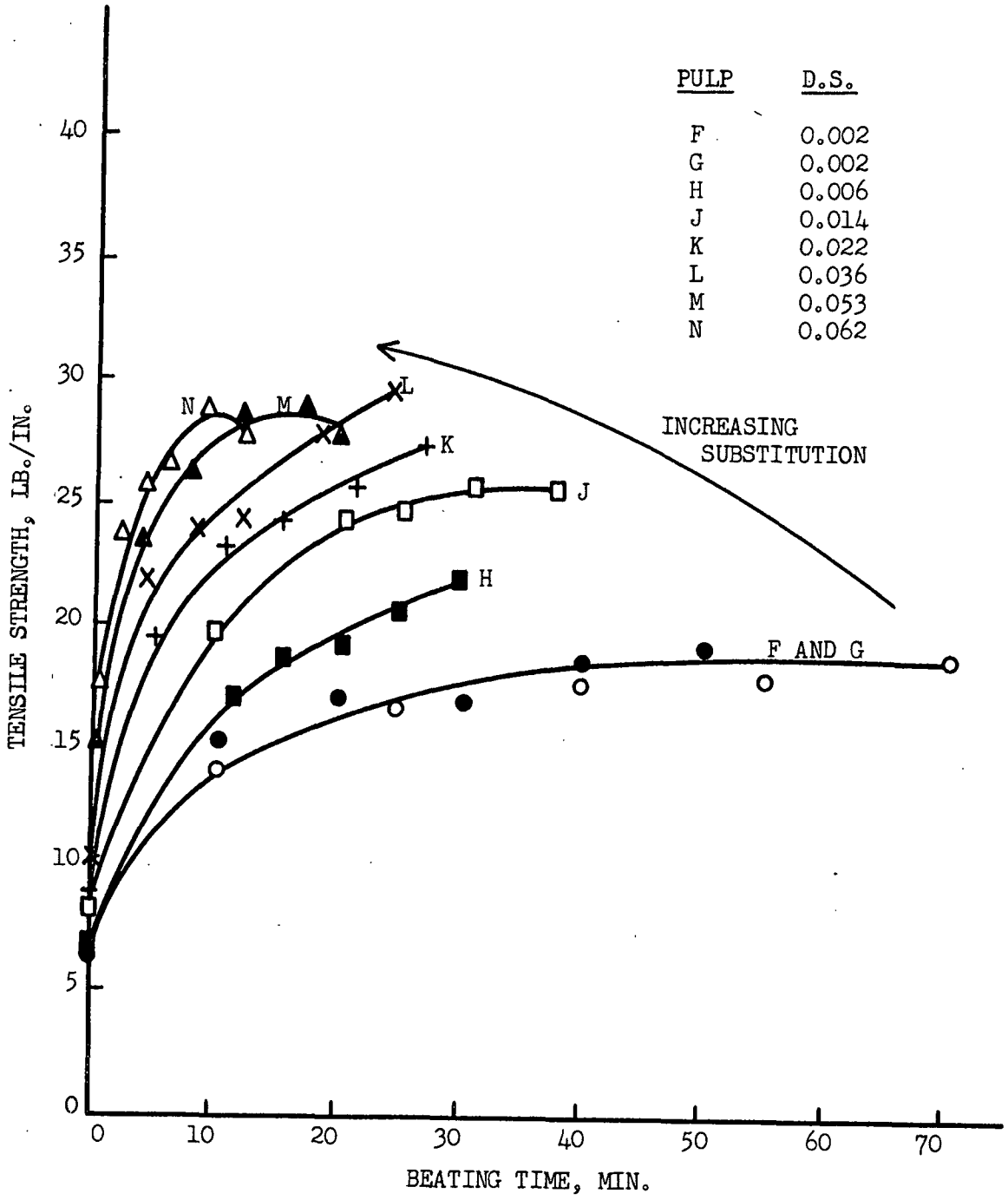

Fig. 9 Tensile Strength versus Beating Time

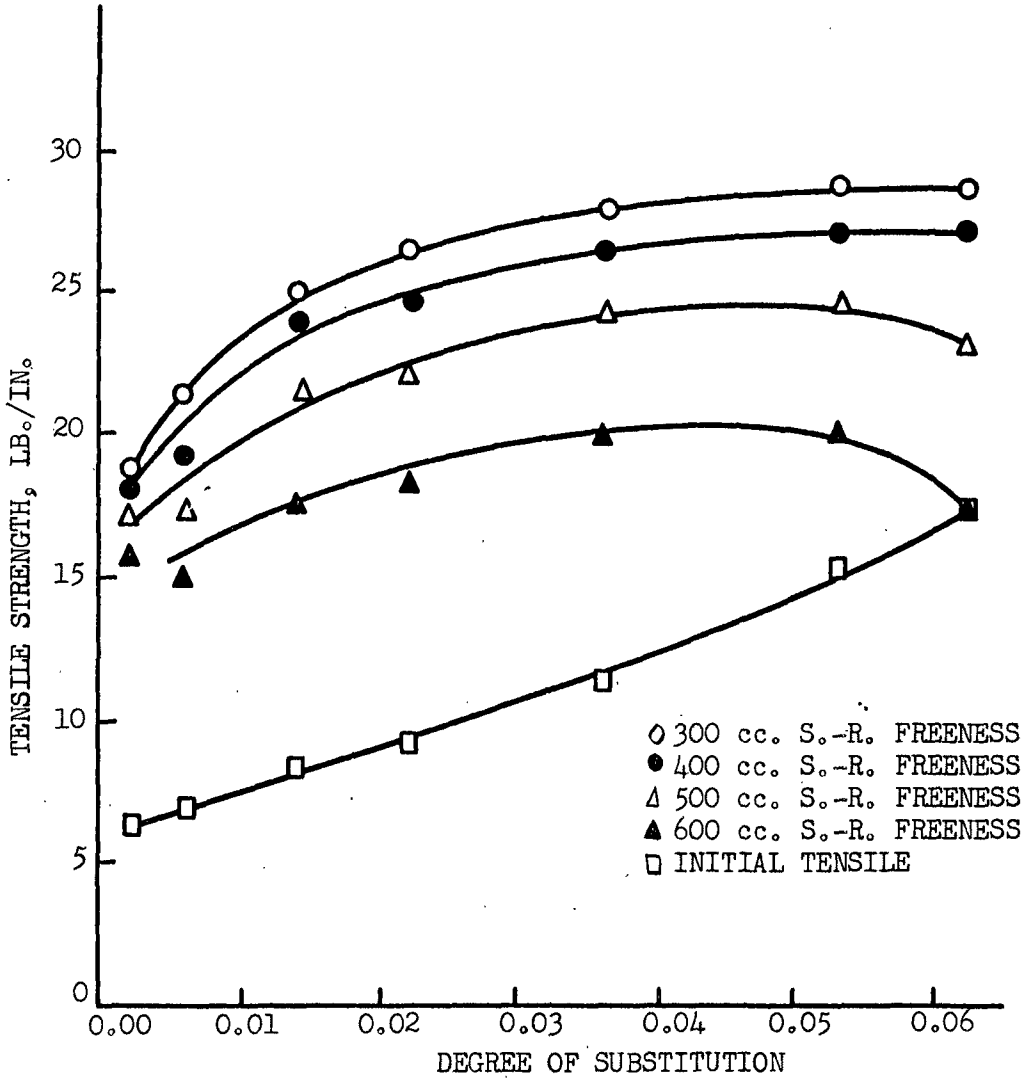

Fig. 10 Tensile Strength versus Degree of Substitution at Constant Freeness

by beating the control pulps. Thus, with an unbeaten (but carboxymethylated) pulp of a Schopper-Riegler freeness in the range 600 to 700 cc. the maximum burst and tensile strengths of the untreated pulps have been equaled and exceeded. Further, the strength increase with beating of these CMC pulps is greater than for the control pulps. Thus, whether the handsheets are compared at a constant beating time, a constant freeness, or a constant apparent density, the burst and tensile strengths are greatly increased by carboxymethylation.

TEARING RESISTANCE

Figure 11 presents the change in tearing strength of handsheets with change in D.S. both at constant freeness and at the initial or zero beater interval. The curves in this figure are only approximate due to the scatter of the points for each curve.

At the low D.S. end, these curves have been drawn to include either the point representing the untreated control pulp (F), or the point representing the treated control pulp (G). In every case the upper point corresponds to the untreated control. This difference between pulps F and G shows that the treatment other than carboxymethylation used in this study adversely affects the tearing properties of the pulp. At the intermediate D.S.'s (Preparations J, K, and L) the tear strength of the untreated control pulp is exceeded for each of the five curves in Figure 11. At the higher D.S.'s the tear strength of the pulp again decreases.

In summary, there is little over-all change in the tear strength of the pulps with carboxymethylation, but there seems to be a slight increase in the tear in a D.S. range of 0.02 to 0.04.

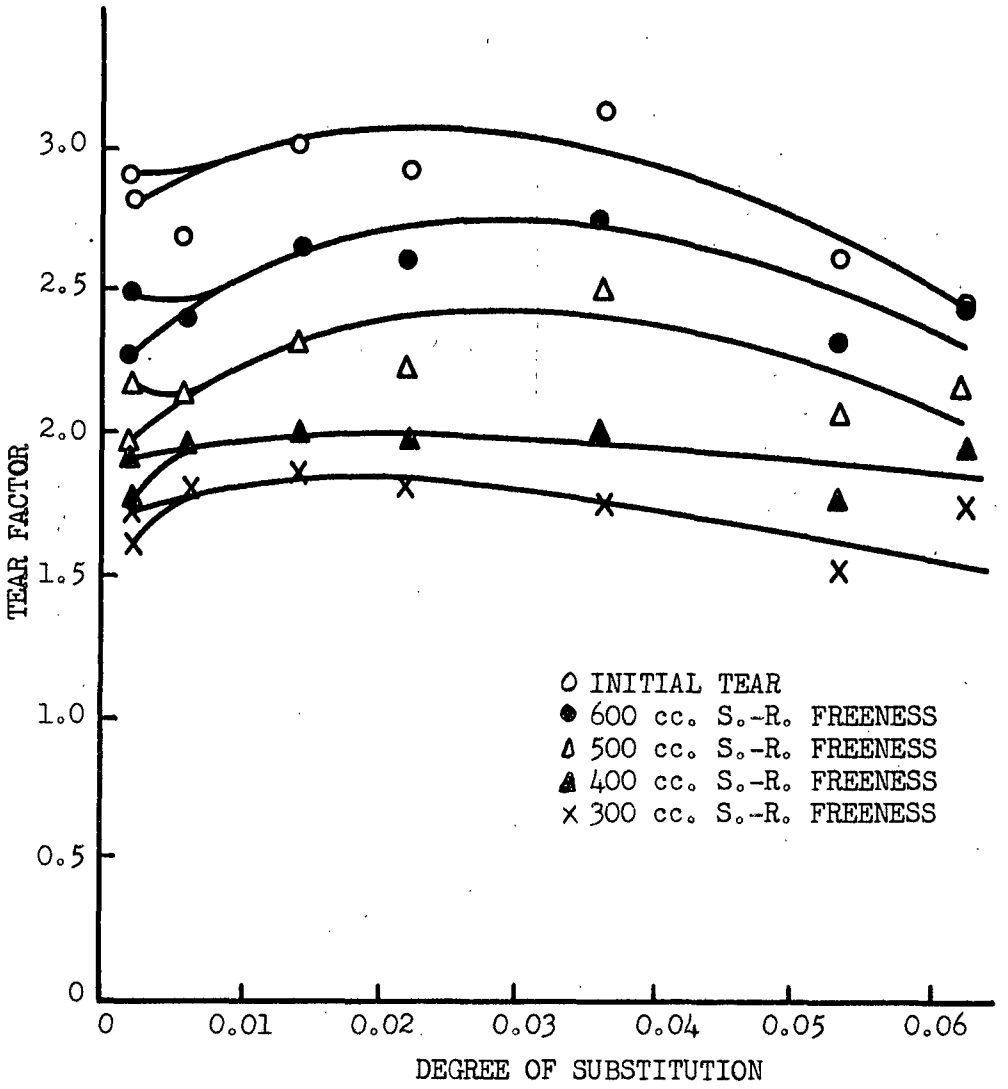

Fig. 11 Tearing Strength versus Degree of Substitution at Constant Freeness

ZERO-SPAN TENSILE

Figure 12 presents the zero-span tensile data for each preparation as a function of beating time. The curve for the untreated control pulp (F) is normal for this test and the points for the treated control pulp (G), although much more scattered, tend to follow this general curve. The increase in zero-span tensile at the short beating times is thought to be due to a compacting of the sheet, allowing the zero-span jaws to obtain a firmer hold on the fibers. After this initial increase, the zero-span tensile values no longer change appreciably with beating.

The remarkable features of these data are that carboxymethylation increases the zero-span tensile of the samples, and that for any given CMC sample the initial increase in zero-span tensile with beating is much greater than for the control samples.

The chief property which this test is supposed to measure is the strength of the individual fibers although the degree of bonding in the sheet plays some role in determining the value obtained (51). The increase in zero-span tensile strength observed with carboxymethylation and with the beating of CMC pulps may be explained in two ways. First, an increase in bonding or bonded area between fibers may allow the jaws of the zero-span tester to obtain a still better grip on the fibers and thus closer approximate their ultimate strength. A second possible explanation is that carboxymethylation and the beating of carboxymethylated fibers actually strengthens the individual fibers through a mechanism either of cross linkage or of reorientation of the cellulose chains in the fibers.

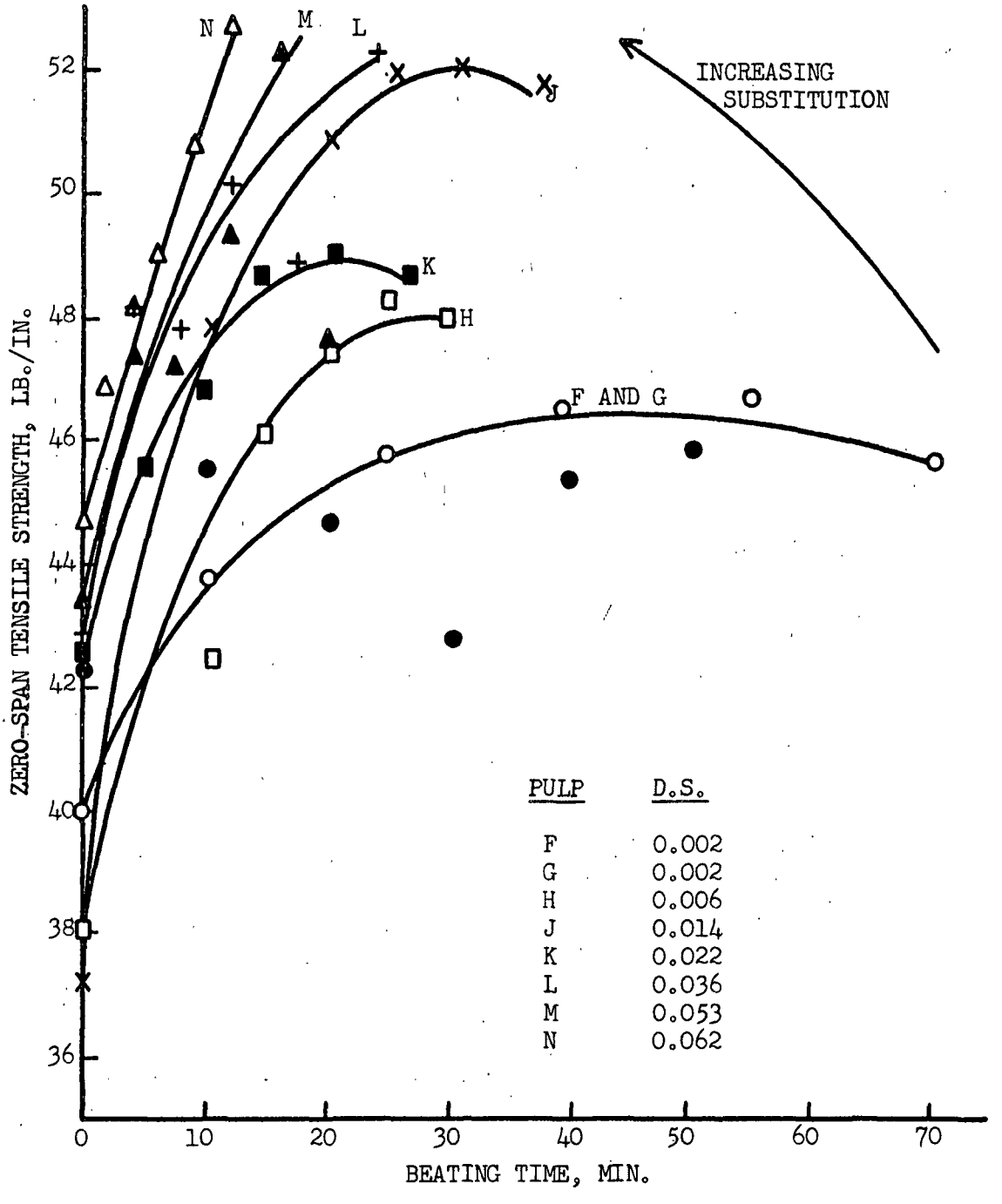

Fig. 12 Zero-Span Tensile Strength versus Beating Time

Both explanations may also be used in an attempt to explain the slight increase in tearing strength mentioned in the previous section. With either better bonding or stronger fibers in a sheet the tearing strength would increase due to the necessity of rupturing more fibers or pulling out longer fibers during the tear.

An exact interpretation of the stronger zero-span tensile values cannot be made but the two possibilities of better bonding or stronger fibers must be considered.

FOLDING ENDURANCE

Figure 13 presents the folding endurance of the handsheets from each preparation as a function of the beating time. It is seen that there is little difference in the folding endurance of the two control samples (F and G). The carboxymethylated samples, however, have improved folding endurances which increase with the D.S. of the sample. At the higher D.S.'s, the initial or zero beater interval samples have folds that are higher than the maximum obtained on the untreated samples.

TAPPI OPACITY

The TAPPI opacity data for this study are presented in Figure 14. There is little or no difference in the TAPPI opacity values for the two control pulps. It is seen, however, that the opacity of the handsheets decreases as the D.S. is increased.

Opacity is usually considered to be a measure of the fiber-to-fiber contacts in a sheet. Two fibers in contact may transmit a ray of light incident upon their point of contact. However, if the fibers are separated, there are two air-fiber interfaces from which the light may be partially reflected.

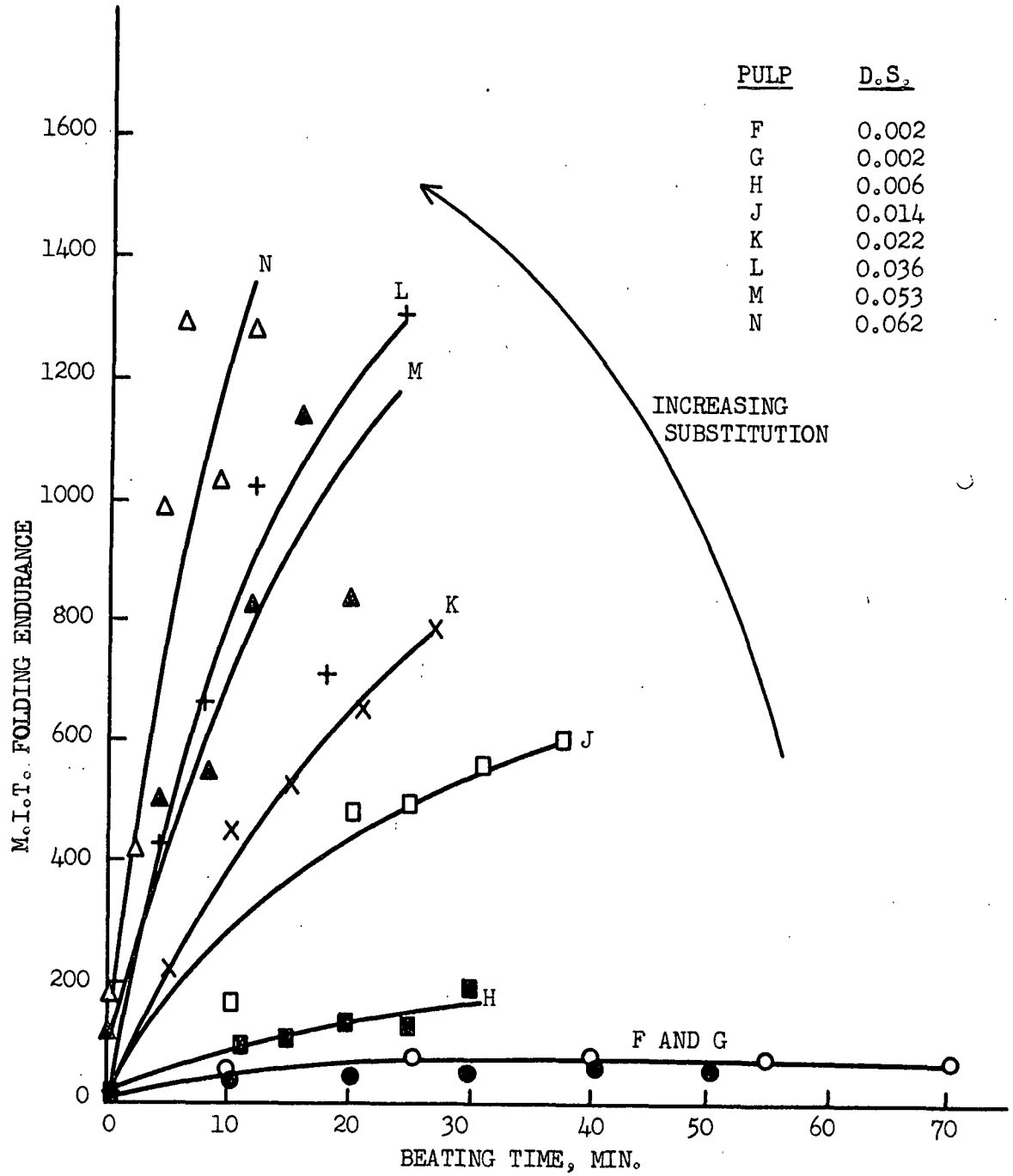

Fig. 13 Folding Endurance versus Beating Time

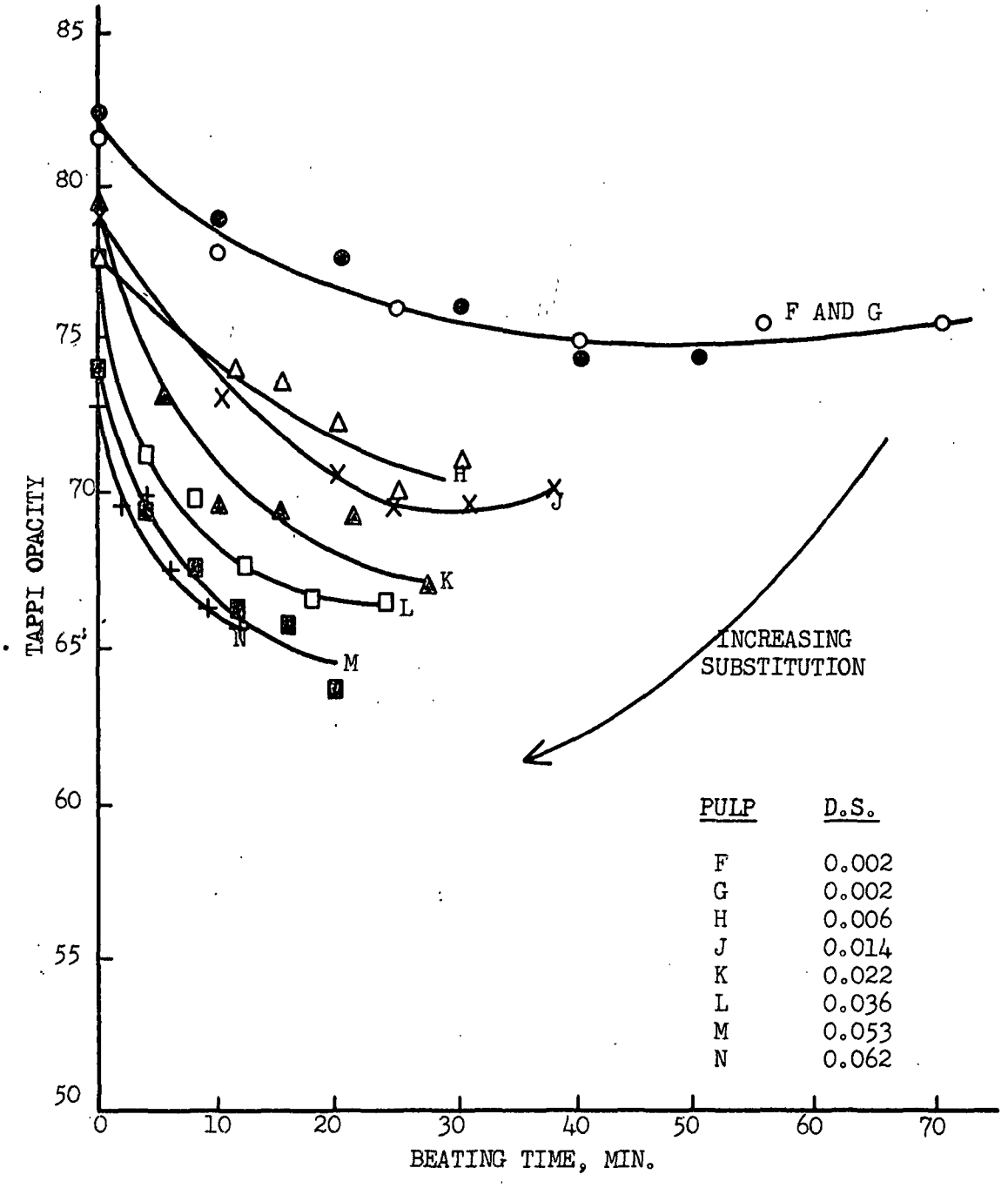

Fig. 14 TAPPI Opacity versus Beating Time

The sheets prepared in this study become less opaque as the D.S. and degree of beating are increased. The apparent density of the sheets with lower opacities and higher D.S.'s are about the same as those of the control pulps, i.e., compared at a constant apparent density the opacity of the sheets decreases with an increasing D.S. This indicates that although the bonded area has been increased in the CMC pulps (lower opacity) the sheet density has remained the same, i.e., the increased bonding has not been achieved through the compacting of the fibers in the sheet. These data would tend to indicate that the fiber structure of the CMC sheet is similar to that of the control sheets but that in the CMC sheets the bonded area has been increased.

Another possible explanation is that the scattering coefficient of the fibers themselves has been changed. This is possible if instead of increasing the fiber-to-fiber bonded area the internal bonding within the fiber itself has been increased by carboxymethylation. In this case, the decrease in opacity observed at a constant apparent density would be due to a decrease in the opacity of the fibers themselves. The photomicrographs, presented later in this section, show a decrease in the opacity of the CMC fibers.

It is likely that both the inter- and intra-fiber bonding is increased by carboxymethylation to obtain the observed decrease in opacity with the increasing D.S.

POROSITY

Figure 15 presents the air porosity data for the handsheets prepared in this study. It is seen that, except for preparation N, carboxymethylation has caused the sheet to become more resistant to the passage of air.

This would indicate that the structure of the sheet has been closed up, due perhaps to the increase in bonded area mentioned in the preceding section.

FIBER CLASSIFICATION

Figure 16 presents some of the fiber classification data obtained in this study. For the several samples compared at a constant pulp freeness, this figure presents the amount of fiber retained on the various screens of the Bauer - McNett classifier. Although the points on this graph show a great deal of scatter the following trends do appear. The CMC pulps have more fiber retained on the 20-mesh screen than do the control pulps and proportionately less on the 35-, 65-, and 150-mesh screens. The amount of pulp retained on all of the screens except the 35-mesh tended to decrease with increasing D.S. On the 35-mesh screen the trend appears to be in the opposite direction.

These changes in fiber classifications show an increase in the longer fiber fraction with carboxymethylation. This is probably due to the fact that since the pulps were compared at a constant freeness the CMC pulps had received considerably less beating (i.e., less time in the Jokro mill) than had the control pulps.

EQUILIBRIUM MOISTURE CONTENT

The moisture contents of the handsheets prepared from each sample and in equilibrium with air at 73°F. and 50% relative humidity are given in Figure 17. It is seen that the equilibrium moisture content of the CMC pulps increases slightly but regularly with increasing D.S.

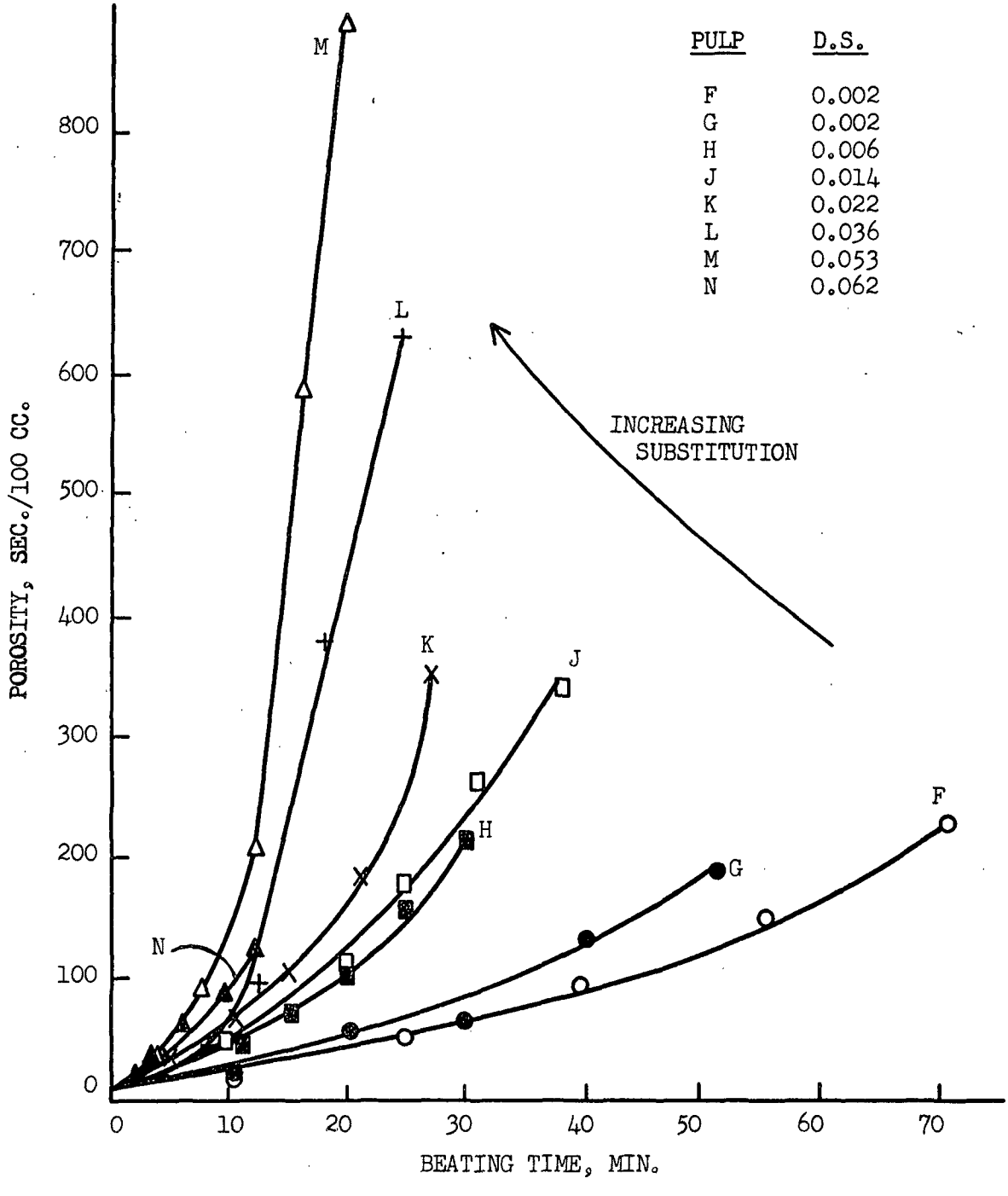

Fig. 15 Porosity versus Beating Time

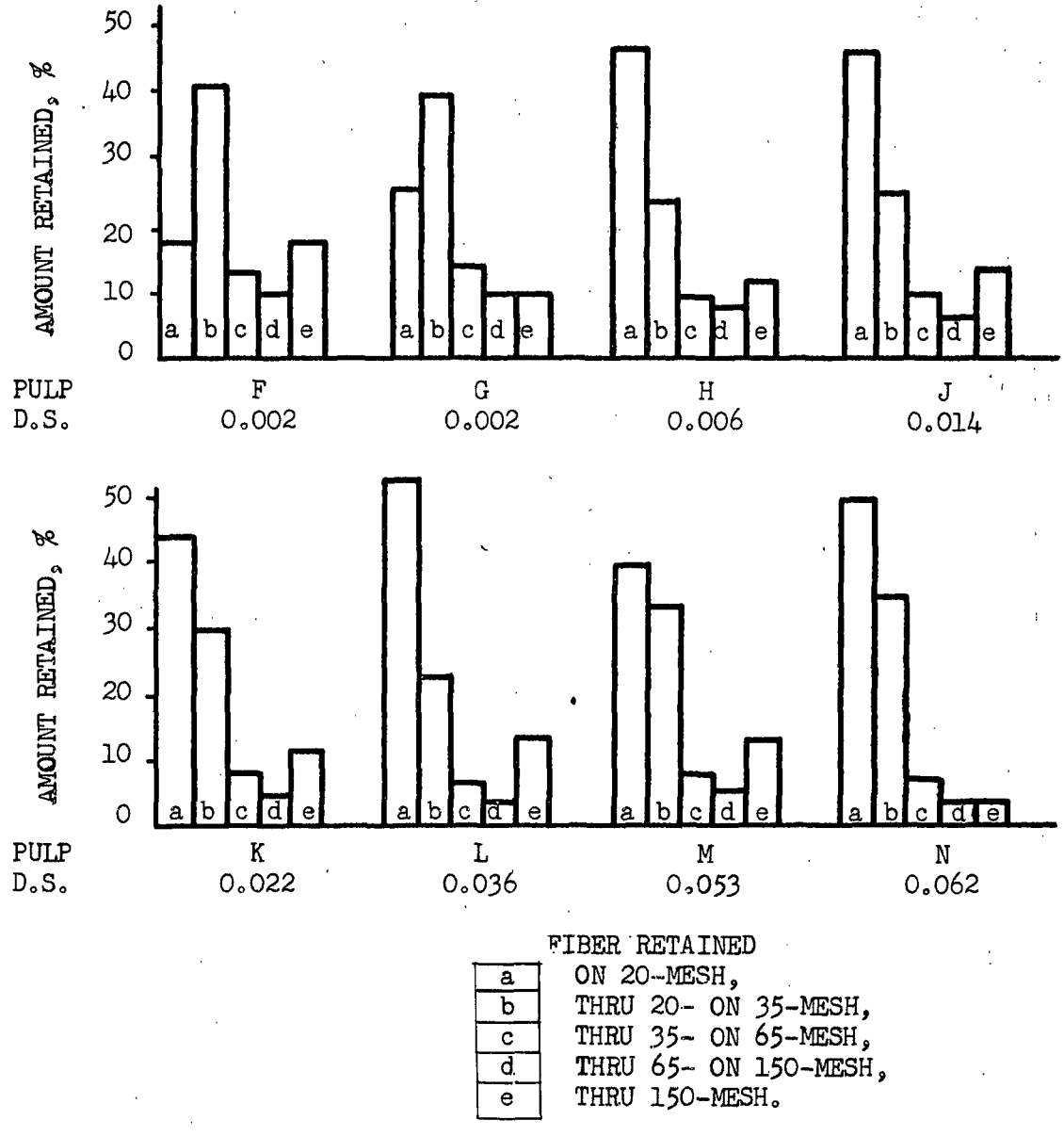

Fig. 16 Fiber Classification at 450 cc. S.-R. Freeness

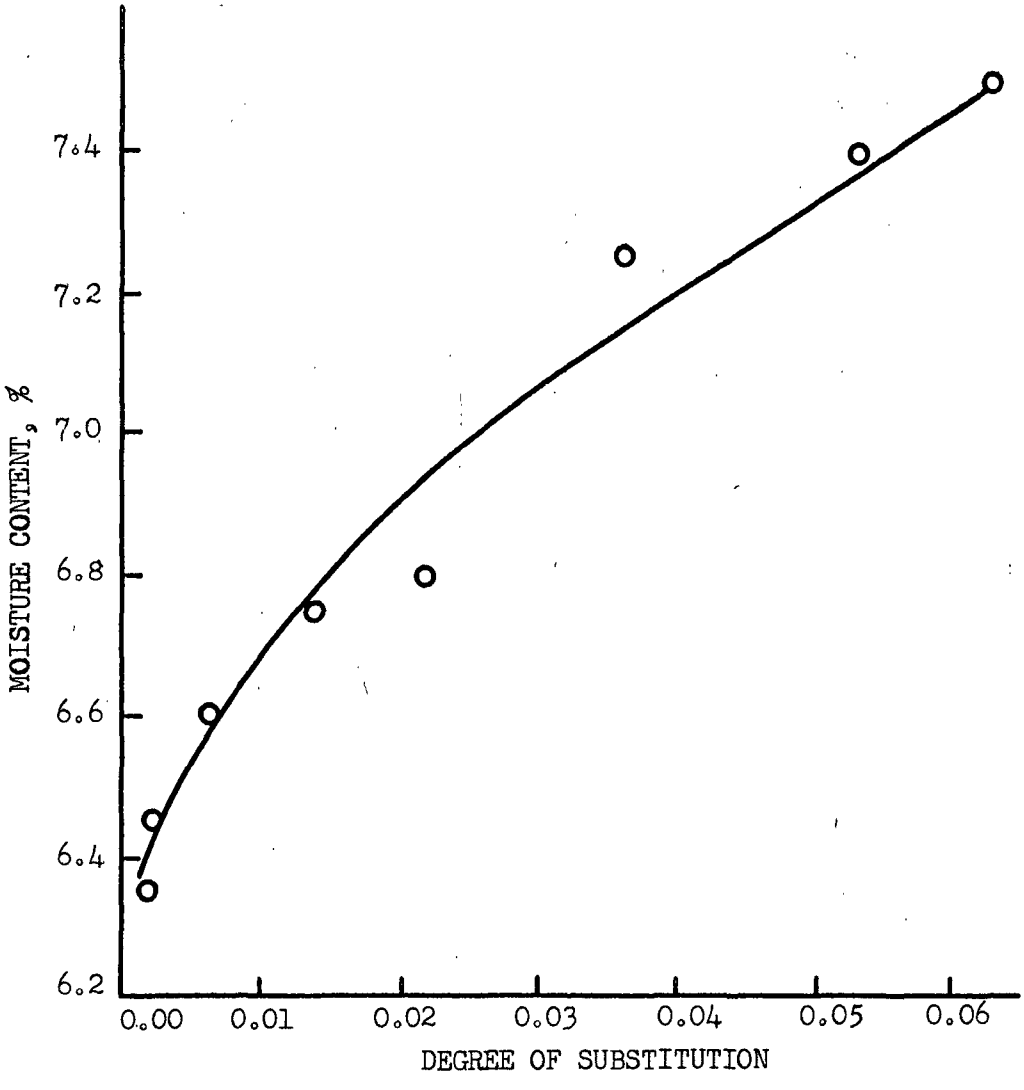

Fig. 17 Relationship of Degree of Substitution to Moisture Content at Standard Conditions

This increase in equilibrium moisture content may be due either to an increased accessibility of the hydroxyl groups of the cellulose or to the hydrophilic nature of the carboxymethyl group substituted for some of the hydroxyl groups.

ACID FORM OF CMC

Table XXI shows the difference in beating and handsheet properties brought about by beating carboxymethylcellulose in the acid form rather than in the sodium-salt form used throughout this work. This data shows that in the sodium-salt form the pulp beats faster. The sodium CMC handsheets also have higher burst and tensile values than handsheets formed from the acid from CMC. The CMC pulps used throughout the rest of this study were in the sodium-salt form to obtain these greater strength increases.

PHOTOMICROGRAPHS

Figures 18 to 25 are photomicrographs of the beaten and unbeaten pulps of the two control preparations (F and G) and the highest-D.S. CMC preparation (N). The observations and interpretations made in this section are based on observations of these fibers under the microscope as well as the photomicrographs.

Consider first, Figures 18, 20, and 22 (magnification of 160 diameters) which are the unbeaten pulps of Preparations F, G, and N respectively. There seems to be little difference in the appearance of the fibers in these three figures. In actual observations under the microscope, it was noted, however, that the fibers of the CMC Preparation N were more transparent than those of either of the control pulps. A close comparison of these figures also shows this trend.

Fig. 18 Preparation F; Untreated Control Pulp; 160X
795 cc. S.-R. Freeness; Unbeaten

Fig. 19 Preparation F; Untreated Control Pulp; 160X
320 cc. S.-R. Freeness

Fig. 20 Preparation G; Treated Control Pulp; 160X
810 cc. S.-R. Freeness

Fig. 21 Preparation G; Treated Control Pulp; 160X
305 cc. S.-R. Freeness

Fig. 22 Preparation N; CMC Pulp of D.S. = 0.062; 160X
600 cc. S.-R. Freeness

Fig. 23 Preparation N; CMC Pulp of D.S. = 0.062; 160X
300 cc. S.-R. Freeness

Fig. 24 Preparation F; Untreated Control Pulp; 110X
320 cc. S.-R. Freeness

Fig. 25 Preparation N; CMC Pulp of D.S. = 0.062; 110X
300 cc. S.-R. Freeness

Figures 19, 21, and 23 (magnification of 160 diameters) show the beaten fibers of Preparations F, G, and N at about 300-cc. Schopper-Riegler freeness. In order to obtain this freeness the untreated control pulp (F) was beaten 85 minutes in the Jokro mill while the treated control pulp (G) was beaten 50 minutes and the CMC pulp (N) was beaten only 12 minutes.

A definite difference may be observed between the beaten CMC pulp and the two control pulps. The CMC fibers appear to be longer, broader, straighter and less twisted than the fibers of either of the control pulps. The ends of the CMC fibers appear broomed or brushed rather than clean cut as do the fiber ends of the control pulps. The CMC fibers are also more transparent than the fibers of the control pulps. The type of fibrillation is different in the two cases. For the control pulps the fibrils are shorter and knottier than those of the CMC pulp. The CMC fibers seemed to be easily split both at the ends of the fibers and along their length. The fibrils formed from the CMC fibers are thinner, more transparent, and appear to be partly soluble, whereas the fibrils formed from the control pulps are more opaque and seem to be a definite part of the fiber.

Figures 24 and 25 are of the same pulps shown in Figures 19 and 23, except that the magnification has been changed from 160 diameters to 110 diameters. These pictures, at a magnification of 110 diameters, show even more clearly some of the changes with carboxymethylation mentioned above.

These photomicrographs show only three of the pulp preparations studied in this investigation and only the unbeaten and fully beaten samples of these preparations. Since the extremes in difference of treatment

were chosen, these photographs show the maximum changes that occurred. It is assumed that the other CMC pulps were altered in a similar manner but to a lesser extent than the high-D.S. CMC pulp (N) pictured here.

DISCUSSION OF RESULTS

A discussion of some of the possible reasons for changes in properties upon carboxymethylation that were noted in this study is contained in this section. This discussion is based on the work and theories of other investigators as well as observations made in this study. The first part of this section is devoted to the development of a theory to explain the action of carboxymethylation on rag pulps, and the second part utilizes this theory to explain the changes in properties observed in this investigation. It must be emphasized, however, that the ideas presented in this section are merely theories. Further research would be required to establish the mechanisms causing the changes in pulp properties that were observed upon carboxymethylation. Some suggestions for an investigation of this sort are presented in this section.

ACTION OF CARBOXYMETHYLATION

The work of Timell (32) indicates that at the low levels of substitution studied in this investigation carboxymethylation does not occur uniformly throughout the cellulose structure but rather is localized in its action, forming areas in the fiber of higher and lower carboxyl contents. Evidence for this localized action was found in the partial solubility of low-D.S. CMC. The soluble portion in every case had a higher D.S. and lower D.P. than the bulk of the cellulosic material.

It may be assumed that carboxymethylation is somewhat localized in this study as well. The pretreatment (water soak and solvent exchange drying) should have opened up some of the interior regions of the cellulose fibers, but it is certain that some areas of the fiber were more accessible to reagents than others. D.S.'s determined on the CMC preparation of the highest D.S. before and after the final washes and sheetmaking showed a slight lowering of the D.S. by this treatment. It may be assumed that this slight lowering in D.S. was due to solution of high D.S. material.

Another indication of localized reaction is found in the relationship of D.S. to time of reaction. While the initial increase in D.S. is rapid (reaction with more accessible regions of the fiber), the D.S. levels off for longer reaction times (slower reaction with less accessible regions and partial solution of high D.S. fractions).

The low-D.S. CMC pulps prepared in this study may be assumed to have carboxymethyl groups distributed throughout the cellulose fiber with local zones of high carboxyl content.

Carboxymethylation very likely alters the cellulose-water relationship of the fiber. The carboxyl group is more hydrophilic than the hydroxyl group that has been replaced and the introduction of carboxymethyl groups probably disrupts the fiber structure, making it less uniform and more easily accessible to water. Thus, in two ways carboxymethylation may increase the affinity of the pulp for water or increase the hydrophilic nature of the fibers.

This increase in the hydrophilic nature of the pulp would occur throughout the fibers and be especially strong in the zones of high carboxyl content. An increase in equilibrium moisture content of the CMC pulps was noted in this study (Figure 17), and the increase in liquid water retained by CMC pulps was noted in this study and by Reid and Daul (36).

This increase in the water retained by these CMC pulps is an indication of increased swelling. An increase in water content and degree of swelling creates a more plastic fiber and one that is easier to fibrillate and beat without cutting. The carboxymethyl groups introduced into these pulps may have an effect similar to the role of naturally occurring hemicelluloses in wood pulps, as described by Cottrall (7). Both hemicelluloses and the carboxymethyl groups substituted in this study are an intrinsic part of the cellulose fiber and are probably located in varying concentrations throughout the fiber. Due to its hydrophilic nature, this part probably increases the amount of water adsorbed by the pulp, the degree of swelling of the fiber, and the plasticity of the fiber, thus permitting easier beating and stronger sheets. Both hemicelluloses and carboxymethyl groups may be located in the interior of the fiber where their increased water adsorption and swelling may cause internal disruption of the fiber and present points of easier fibrillation.

Beating of carboxymethylated fibers is probably facilitated due to their more plastic or less brash nature. Beating tends to fibrillate the CMC pulp both externally and internally. As mentioned above, the carboxymethyl groups located in the interior of the fiber may make fibrillation easier by presenting disrupted zones in the fiber structure. The fibrils formed from CMC may also tend to be more plastic and partly soluble due to the carboxymethyl groups substituted on them. Further, due to the more

swollen and plastic nature of the interior of the fibers theorized above, internal fibrillation may be facilitated as well.

Upon drying a sheet of partially carboxymethylated fibers, bonding appears to be greater than for untreated fibers. The more soluble and plastic nature of the fibrils and other exterior surfaces of the CMC fibers suggested above would permit greater bonded areas than for untreated fibers. Also beating would result in an opening up of greater surface areas to provide more hydroxyl groups for interfiber bonding.

It should also be noted that internal fibrillation in CMC fibers and the more soluble character of the interior of the fibers mentioned previously would bring about an increase in bonding between cellulose chains within the fiber. This bonding within the fiber would create a more uniform structure, filling in some of the voids in the fiber and creating a stronger cellulosic fiber.

Carboxymethyl groups introduced into cellulose fibers may thus increase the degree of swelling of the fiber and open the fiber structure, permitting easier beating and the formation of stronger paper through the formation of larger bonded areas both within and between fibers.

A remark made by Cottrall, mentioned earlier, is: (11) "If you could introduce hemicellulose in pulp and chain it up to the fiber, as it were, I think then you would get this increased strength." In a sense this may have been done by carboxymethylation. Part of the cellulose chain in the fiber has been altered so that a type of hemicellulose has been produced.

Jayme (1), Bletzinger (2), Aiken (3), and Harrison (4) have produced pulps with increased hydrophilic properties by methylation and acetylation. This increase in hydrophilic properties was attributed to an opening up of the cellulose structure of the fibers to make more hydroxyl groups available for water adsorption and bonding. This same mechanism probably plays a role during carboxymethylation. There is a difference, however, for with increased substitution of methyl or acetyl groups the pulp is no longer wet by water. The carboxymethyl group, on the other hand, is hydrophilic; and increased substitution produces a water-soluble, cellulosic product. Thus, besides the opening up of the cellulose structure, which probably occurs when either hydrophilic or hydrophobic groups are substituted in small amounts, the carboxymethyl group has the property of adding its hydrophilic nature to the cellulose.

The CMC pulps prepared in this study should also be differentiated from the use of CMC as a beater additive. With beater additives, any change in properties probably takes place at the fiber surface where the beater additives may increase the hydrophilic nature of the surface and aid in bonding. Being adsorbed at the surface, a beater additive may be removed by washing. For CMC pulps, on the other hand, the carboxymethyl groups are fixed to the cellulose fibers and are probably located throughout the fiber, rather than only on the surface.

INTERPRETATION OF RESULTS

Preceding paragraphs have described the experimental results obtained in this study, and an attempt has been made to devise a theory to explain the changes in cellulose fibers brought about by carboxymethylation.

Although further study would be required to prove or disprove the ideas presented in this theory, it is of interest to see to what extent this theory explains the changes in pulp properties due to carboxymethylation observed in this study.

It was noted previously that the TAPPI opacity of handsheets decreased with increasing D.S. when compared at a constant apparent density. This decrease was attributed to either increasing inter- or intrafiber bonding or both. It is possible that carboxymethylation alters the fiber structure permitting both better inter- and intrafiber bonding. Interior fibrillation and increased solubility of CMC fibers would create more uniform fibers by filling some of the fiber voids and causing increased bonding between cellulose chains when the fiber is dried.

A change in the interior of the fiber may be shown in other ways. When the fibers are observed under the microscope the CMC fibers are more transparent than the untreated fibers. This transparency indicated a more uniform interior fiber structure, for nonuniformities and voids in the interior of the fiber present points at which light may be scattered and thus create a more opaque fiber. When these voids and nonuniformities are filled, due perhaps to the partial solubility and internal plasticity of the CMC fibers, the fiber becomes more transparent.

The increase in the zero-span tensile strength of the fibers with carboxymethylation and the greater increase in zero-span tensile upon beating of the carboxymethylated fibers also indicates a change in the interior structure of the CMC fibers. Here again an increased solubility and plasticity of the interior of CMC fibers, allowing for a more uniform and more bonded structure, may explain the increased strength. Also,

since beating may increase the internal fibrillation and plasticity of the CMC fibers more than the untreated fibers, the greater increase in zero-span tensile of the CMC fibers with beating may be due to improved intra-fiber bonding.

This increase in the zero-span tensile strength of the CMC sheets occurs even though the D.P.'s of the pulps have been lowered from about 2000 to about 1000. Although the final D.P. of 1000 is not low enough to cause a severe loss in fiber or paper strength, it is of interest to note that the physical strength properties of the CMC fibers and handsheets have been increased over those of the untreated pulp in spite of their lowered D.P.

Thus, there is some evidence that carboxymethylation alters cellulosic fibers so that they are more uniform and have increased bonding between cellulose chains. These changes produce a fiber that is more transparent and stronger than the untreated fiber.

This increase in transparency and strength of the fibers points to an increase in intrafiber bonding due to carboxymethylation. An increase in interfiber bonding probably also occurs. As was mentioned earlier carboxy-methylation is a localized reaction and the exterior of the fiber is accessible to the reagents during the preparation. Also beating tends to open the interior of the fiber making greater areas accessible for inter-fiber bonding. It seems probable that carboxymethylation has changed the exterior of the fiber producing a surface that is softer, partly soluble in water, and more easily bonded to other fibers.

A change in the surface of the fiber is indicated in the photomicrographs of the beaten fibers. The fibrils of the untreated fibers are coarse and short and have been produced only after long treatment in the Jokro mill. With the carboxymethylated fibers however, fibrillation occurred with much less beating. The CMC fibrils appear longer and more transparent and at some points approach the appearance of a slime.

CMC pulps are beaten to a given freeness in less time and when compared at a given freeness have longer fibers than untreated pulps. This is a further indication that carboxymethylation has softened and plasticized both the exterior and interior of the fibers making the fibers easier to fibrillate and less liable to the cutting action of the Jokro mill.

The changes in many of the physical properties of handsheets made of CMC fibers may be attributed to increased inter- and intrafiber bonding. The increases observed in bursting, tensile, and folding strength may all be attributed to stronger bonds between stronger fibers. Increased bonding between fibers would also cause the observed decrease in sheet porosity with increasing D.S. Increased bonding would affect the tearing strength in two ways. The stronger bonded sheet with stronger fibers tends to increase the tearing strength of the CMC sheets. At the same time the increased bonding in the sheet limits and compacts the zone over which the tearing forces may act, tending to lower the tearing strength of the CMC sheets. The result of these two effects may be little or no change in the tearing strength of the sheets due to carboxymethylation.

The properties of handsheets made from CMC pulps with no treatment in the Jokro mill (zero beating interval) are also of interest. The

bursting strength, tearing strength, and folding endurance of these zero beater interval handsheets from pulps of high substitution exceed those of sheets from the beaten but uncarboxymethylated pulps. The tensile strength and TAPPI opacity of these CMC sheets is only slightly lower than that of the sheets from the beaten but untreated pulps and the CMC pulps have a much higher Schopper-Riegler freeness and form sheets of a much lower apparent density. Thus, carboxymethylation has altered the rag fiber so that the strength properties of handsheets from well beaten but untreated rag fiber are equaled and exceeded with little or no mechanical treatment of the CMC fibers and with a pulp of a much higher freeness. This is further evidence that the exterior of the fibers has been altered to permit better bonding between fibers, for without beating to produce fibrillation it is only the exterior of the fiber that is available for bonding.

Bletzinger (2) found that at the zero beater interval the substituted acetyl pulps of low D.S. showed a decrease in strength properties and beating was required to develop the increases that he observed. He theorized that external hydroxyl groups had been covered leaving fewer available for bonding. In this study the addition of carboxymethyl groups to the surface of the fiber does not seem to inhibit bonding but rather enhances it by making the fiber surface softer and more soluble even at the zero beater interval.

It was mentioned earlier that the change in properties with carboxymethylation seems to be most rapid up to a D.S. of about 0.03, while above this point additional substitution does not cause as great a change in properties. Also in some cases at the higher D.S.'s there is a decrease in some properties that had been high at intermediate D.S.'s. There seems to

be an optimum D.S. at about 0.03. This change in the effect of carboxymethylation may be explained on the basis of the ideas that have been presented. Since carboxymethylation is a somewhat localized reaction, it will be the regions of the fiber that are most accessible to the reagents that react first. These regions would probably be the exterior of the fiber and the most highly disordered regions of the interior of the fiber. These are the very regions where carboxymethylation may be of the greatest aid in bonding. Carboxymethylation of the exterior of the fiber probably promotes bonding between fibers, while carboxymethylation of the most disordered regions of the interior of the fibers very likely promotes reorientation and bonding between cellulose molecules in the weakest zones of the interior of the fiber. Further, carboxymethylation probably increases the D.S. of the accessible regions and brings about the substitution of some of the less accessible regions of the fiber. Up to a point, this may aid in the bonding mentioned above; but beyond this, continued substitution would place carboxymethyl groups in the regions of the interior of the fiber where they would be of no use in aiding bonding, either within or between fibers. Also, as the substitution continues, some of the CMC becomes highly substituted and water soluble and may be dissolved away from the surface and interior of the fiber. If this occurs, although the D.S. of the entire fiber continues to increase due to substitution elsewhere in the fiber, it is the carboxymethyl groups of importance to bonding that are removed, leaving weaker fibers and a weaker sheet.

FUTURE WORK

A theory has been presented in the preceeding paragraphs to explain the action of carboxymethylation on rag pulps and to explain the changes

in papermaking properties due to carboxymethylation observed in this study. Further work would be required to determine if this suggested theory is correct. Some determinations that would be of interest are: (a) single fiber tensile strengths to determine if the strengths of the individual fibers are actually increased by carboxymethylation, (b) x-ray diffraction patterns to determine if the amounts or type of crystallinity in the fiber has been changed by carboxymethylation, (c) the scattering coefficient of normal and acetone - butanol handsheets to determine the change in bonded area due to carboxymethylation, (d) Thwing formation determinations to determine if the formation of sheets from CMC pulps are better than sheets of untreated pulp, (e) bonding strength determinations using the Institute of Paper Chemistry's bonding strength tester, (f) equilibrium water - vapor isotherms, (g) uniformity of substitution, (h) the degree and heats of swelling in various media and (i) the surface areas of both beaten and unbeaten samples.

The properties of these CMC pulps would be of interest commercially if the method of preparation was feasible on a commercial scale. Since the method of preparation used is probably not commercially feasible a search for other methods to prepare CMC pulps with similar properties would be of interest. Also, since other groups such as the carboxyethyl, hydroxyethyl, and phosphoric acid groups are hydrophilic in nature and may be substituted on cellulose, a study of the preparation and papermaking properties of their cellulosic derivatives would be of value.

It is possible that the surface of this field has only been scratched and by producing various cellulosic derivatives, papermaking pulps of unique and useful properties may be obtained.

SUMMARY AND CONCLUSIONS

CARBOXYMETHYLCELLULOSE PREPARATION

1. A method of preparing CMC pulps up to a D.S. of 0.070 has been devised and studied. There are four steps in this method. (a) Pretreatment: The airdry rag pulp is soaked in water and then solvent exchange-dried from either methyl alcohol or benzene. (b) Acid Treatment: The pretreated pulp is soaked for 10 to 120 minutes in an isopropyl alcohol solution of chloroacetic acid (0 to 30 grams/100 cc.). (c) Substitution: The acid-soaked pulp is placed in an alcoholic sodium hydroxide solution (0.1 to 3.5%) and maintained at the boiling point for 1/4 to 7 hours. (d) Washing: The reaction slurry is neutralized with dilute aqueous acetic acid and thoroughly washed with water. The following statements hold only for this procedure.

2. Higher - D.S. CMC pulps are obtained by using a rag pulp that has been pretreated by soaking in water and air drying from absolute methyl alcohol than by using the original airdry rag pulp. Still higher D.S.'s are obtainable if the pulp is air dried from benzene rather than methyl alcohol.

3. The D.S. of a CMC pulp is a function of the chloroacetic acid concentration used in its preparation but is not affected by the length of the acid treatment.

4. The chloroacetic acid treatment used as one step in the preparation of these CMC pulps does not degrade, mercerize, or carboxymethylate the rag pulps.

5. The D.S. of the CMC pulp obtained is highest when low concentrations of sodium hydroxide (less than 1%) are used in the substitution reaction during its preparation. Less degradation also occurs when low sodium hydroxide concentrations are used.

6. The substitution reaction is essentially completed after one hour at reflux temperatures of 78 to 82°C.

7. The pulps in this thesis are not mercerized by the alcoholic-alkali treatment which they receive during the substitution reaction.

8. The various neutralization and wash procedures studied in this thesis did not significantly affect the viscosity or the D.S. of the resulting CMC pulps.

9. A series of six CMC pulps with D.S.'s from 0.006 to 0.062 and two control pulps were prepared in quantities sufficient for the determination of their papermaking properties.

10. The rag pulp used to prepare these six CMC pulps was degraded from a D.P. of about 2000 for the original pulp to a D.P. in the range 900 to 1300 during the preparation of CMC.

11. There is only a slight loss in the carboxymethyl content of the CMC fibers during beating and handsheet formation.

PAPERMAKING PROPERTIES OF CMC PULPS

Carboxymethylation of rag pulps has produced pulps that have higher strength properties than the untreated rag pulps and achieve these strengths

with less beating. In this study an optimum D.S. seemed to exist at about 0.030. Carboxymethylation up to this D.S. causes a rapid increase in the burst and tensile strengths as well as causing a slight increase in the tearing strength of handsheets prepared from the CMC pulps. Above this D.S. the further increase in burst and tensile strengths with continued carboxymethylation was only slight, and the tearing strength seemed to decrease slightly.

The results of this study of the papermaking properties of a series of CMC pulps prepared for this thesis are summarized below. In these statements, handsheet properties were compared for sheets of the same apparent density or for sheets prepared from pulps of the same freeness. As noted earlier (page 57), for this study the comparison of handsheet properties at constant apparent density is approximately equivalent to the same comparison at a constant pulp freeness.

1. The beating time required to obtain a pulp of a given freeness decreased as the carboxymethyl content of the pulp was increased.

2. The burst and tensile strength and the folding endurance of handsheets in this study increased as the carboxymethyl content of the pulp from which the handsheets were made was increased.

3. The tearing strength of handsheets in this study varied only slightly with the carboxymethyl content of the pulp from which the handsheets were made. A slight maximum in tearing strength was observed, however, in the D.S. range from 0.020 to 0.040.

4. The zero-span tensile strengths of handsheets and the initial increase in zero-span tensile strength with beating both increased as the carboxymethyl content of the pulp was increased.

5. The opacity of handsheets in this study decreased as the D.S. of the pulp from which the handsheets were formed was increased.

6. The porosity of handsheets in this study decreased as the D.S. of the pulp from which the handsheets were formed was increased.

7. The equilibrium moisture content of handsheets at 73°F. and 50% relative humidity increased as the D.S. of the pulp from which the handsheets were formed was increased.

8. Photomicrographs have shown that the beaten CMC fibers have retained more of their initial length and are broader, straighter, and more transparent than the fibers of the untreated pulps beaten to the same freeness.

9. Photomicrographs have shown that the fibrils formed from CMC pulps are longer and more transparent than fibrils formed in untreated pulps.

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APPENDIX

CALCULATION OF D.S. BY SILVER-o-NITROPHENOLATE METHOD

Let CM = carboxymethyl group,
cell = cellulose,
eq = equivalents.
N = normality of KCNS solution.
Let C = eq of Ag/g. CMC = eq of CM/g. CMC.

$$C = \frac{2[(\text{ml. KCNS for blank}) - (\text{ml. KCNS for aliquot})](N)}{(\text{sample weight in grams})(1000)}$$

$$\text{D.S.} = C \times \frac{162 + 58\ \text{D.S.}}{162} \times 162$$

$$\text{D.S.} = \frac{162C}{1 - 58C}$$

Where: D.S. = eq CM/eq cell = Degree of Substitution,

162 = g. cell/eq cell = Equivalent weight of glucose residue,

58 = g. CM/eq CM = Equivalent weight added by substitution of carboxymethyl group,

$\frac{162 + 58\ \text{D.S.}}{162}$ = g. CMC/g. cell = Gravimetric factor.

Sample Calculation:

Assume: 0.5000 gr. sample.
25-ml. blank = 20.00 cc. of 0.011 N-KCNS,
25-ml. aliquot = 10.00 cc. of 0.011 N-KCNS.

$$C = \frac{(2)(20.00-10.00)(0.011)}{(0.5000)(1000)} = 0.00044$$

$$\text{D.S.} = \frac{(162)(0.00044)}{1 - 58(0.00044)} = \frac{(162)(0.00044)}{(0.9745)}$$

D.S. = 0.073